Division of Science and Engineering

Department of Chemical Engineering

Advance Water Abatement in Oil and Gas Reservoir

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Declaration

This thesis contains no material, which has been accepted for the award of any other degree or diploma in any university.

To the best of my knowledge and belief, this thesis contains no material previously published by other person except where due acknowledge has been made.

Signature……..

Date……

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Abstract

The control of excessive water production in oil and gas producing wells is of increasing importance to the field operator, primarily when trying to maintain the survivability of a mature field from shut in. During the last two decades many chemicals have been studied and applied under the name of relative permeability modifier (RPM) to combat this problem. These chemicals were mostly bullheaded individually into the affected zones, consequently their application resulted in low to medium success, particularly in treating reservoirs suffering from matrix flow.

It has been found that the disproportionate permeability reduction depends on the amount of polymer dispersed or absorbed by the porous rock. If single polymers are employed to treat excessive water production in a matrix reservoir they cannot penetrate deep into the formation rock because the polymer will start to build as a layer on the surface of the rock grains. As a result the placement of polymer into the formation will no be piston like and the dispersion over the rock pores will be uneven. To improve water shutoff technology a method of injecting chemicals sequentially is recommended provided that the chemical's viscosity is increasing successively with the chemicals injected.

Experimentally confirmed, injecting chemicals sequentially provides better results for conformance control. The value of post treatment water mobility is conspicuously lowered by the method of applying injecting chemicals sequentially in comparison with the single chemical injection method. For instance, the residual resistance factor to water (F_{rrw}) at the first cycle of brine flushing for this method is approximately five times higher than the F_{rrw} obtained by injecting only one single chemical. Furthermore, for the second cycle of brine flushing F_{rrw} is still higher by a ratio of about 2.5. In addition to this improvement residual resistance factor to oil F_{rro} for this method is less than two which has been considered as the upper limit for conformance control in matrix reservoir. Accordingly injecting chemical sequentially can be applied for enhancing relative permeability modifier performance in matrix reservoir.

Nomenclature

Symbol

Ka	Air permeability
Kw	Absolute water permeability
Q	Volume of water produced
Δp	Pressure difference across the core sample
L=	Sample length, cm
$u =$	Flow rate, cm^3 per second
A=	Cross sectional area,
Kh	Horizontal permeability
μ	Viscosity of the injected fluid
r_e	Drainage radius
r_w	Wellbore radius
ϕ	Porosity, volume fraction
RQI	Reservoir quality index, μm
NPI	Normalized porosity index
FZI	Flow zone indicator
XI	Normalized-cumulative sum of RQI
w/w	Percentage solution
$f(\Delta)$	Permeability percent reduction $\{100 \times (K_{before} - K_{after}) / K_{before}\}$
M	Mobility ratio

Abbreviation

Kw@Sor	Effective water permeability at residual oil saturation
Ko@Swi	Effective oil permeability at residual water saturation
Kw1	Water permeability after chemical treatment
Kw2	Water permeability after Ko1
Kw3	Water permeability at 125 ^{0}C after chemical treatment
Ko1	Oil permeability after chemical treatment
PAM	Anionic polymer
HAPAM	Neutral polymer
CAT	Cationic polymer
PRP	Permeability percent reduction
RPM	Relative permeability modifier
DPR	Disorientate permeability reduction
TDS	Total dissolved solid
F_{rrw}	Residual resistance factor to water
F_{rro}	Residual resistance factor to oil
RF	Resistance factor
Psi	Gauge pressure

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Chapter 1

Introduction

Excessive water production can be defined as the undesired water produced from hydrocarbon wells either on initial completion or after they have been producing for sometime. Many, if not most wells have been shutoff prematurely because of the water handling cost. It is a problem of paramount importance from technical, environmental and oil production points of view (Amanullah 2006). The remedy of excessive water production costs worldwide 40US$ billion annually, whereas in the U.S the disposing cost of this water is estimated to be $5-10 billion (Bailey et al 2000). These costs include the expense to lift, dispose or re-inject, and the capital cost of surface facility construction to ensure that environmental regulations are met (Halliburton 1996).

The demand for effective technology that can selectively control water in situ is urgent, as fields tend to maturity and decline. Investigations have been focusing on prevent water production rather than handling it at the surface. Acrylamide polymers have been recognized as relative permeability modifier in porous medium since early 1964 (Sandiford 1964), various water soluble polymers systems and chemicals have since been studied under the name of relative permeability modifiers (RPM). Today RPM are recognized to be the most suitable solution for preventing water in situ and they have been acknowledged by the oil industry as the valid and economic alternative technique over mechanical isolation for conformance control.

The process of water control by RPM consists of placing a skin of chemicals near the wellbore region for selectively reducing water flows, reserving pressure decline, and increasing sweep efficiency. Water control therefore should not be seen only in terms of incremental oil production, which is often the case, but also in terms of reduction of operating costs associated with water production, both material and environmental (Kume 2003).

Although water control by RPM is often preferred over mechanical isolation, its success in the field has shown moderate success. This is due to poor identification of the:

1- Source of water influx,
2- Chemical selection,
3- Candidate well,
4- Method for field application, and
5- Reliable method to predict actual job post-treatment performance.

A successful treatment by a relative permeability modifier in the field can be achieved whenever the above points are met. Thus, battling excess water production needs a precise plan and strategy. It starts with correctly diagnosing the source, nature, and the mechanism on how water flows into the wellbore region (Seright & Sydansk 2003). Any subsequent design of a water shutoff process requires laboratory experiments, numerical simulations and on-field adjustments (Zaitoun et al 1989). Through this research work, laboratory experiment and proposing new method of injecting chemicals sequentially are presented to mitigate excessive water production in matricial reservoirs.

1-1 Identification of the problems nature:

Most reservoirs that are subjected to an active aquifer will experience water encroachment after they have been producing for sometime. Seright and Sydansk (2003, p. 159) recognized two types of water exist as excessive water production. The first type, usually occurring later in the life of a water flood, is water that is co-produced with oil as part of the oils' fractional flow. If the water permeability decreases, the oil permeability will decrease correspondingly. The second type is water usually flowing to the wellbore by a path separate from that for the oil;

for example, water coning or a high permeability channel through the oil strata (See Fig 1.1). For the second type, reducing water production can lead to greater pressure drawdown and increased oil production rates.

However as the source of water influxes into the producing wells are different, many treatments to approach optimum solution have been studied. Depending on the nature of excess water production, Seright and Sydansk(2003, p. 159) classified water shutoff techniques as chemical and mechanical methods (See Table 1.1). Each of these methods may be effective for certain types of water problems but are usually ineffective for other problems (See Table 1.2).

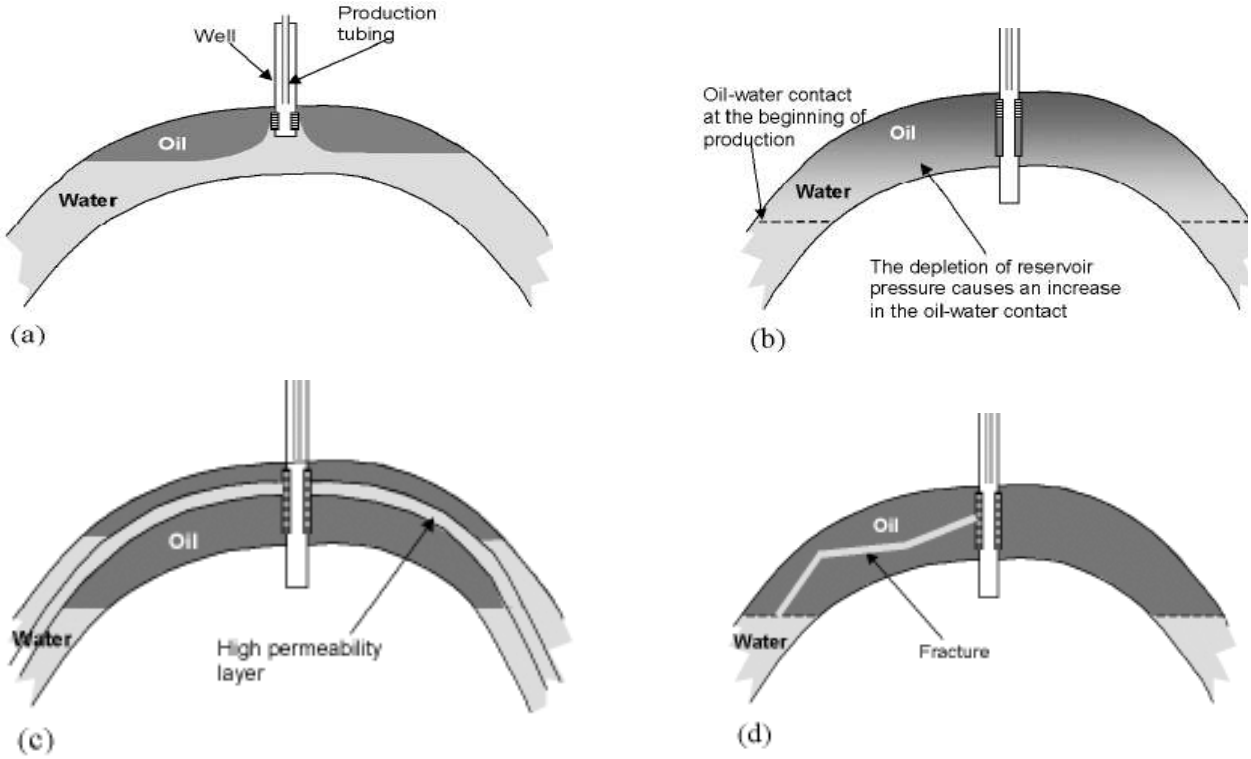


Figure 1.1: Mechanisms by which water can arrive at a production well. After **Mennella et al (1998).

Table 1.1: Water shutoff materials and methods. After Seright & Sydansk (2003).

Chemical and Physical Plugging Agents	Mechanical and well techniques
Cement, sand, calcium carbonate Gel, resins Foam, emulsion, particulate, precipitates, microorganisms Polymer/mobility-control floods	Packers, bridge plugs, patches Well abandonment, infill drilling Pattern flow control Horizontal wells

Table 1.2: Excess water production problems and treatments categories. After Seright & Sydansk (2003).

(*Categories are listed in increasing order of treatment difficulty*)
A-"Conventional" treatments are normally an effective choice: 1-Casing leaks without flow restrictions. 2-Flow behind pipe without flow restrictions. 3-Unfractured wells (injectors or producers) with effective barriers to crossflow.
B-Treatments with Gelants normally are an effective choice. 1-Casing leaks with flow restrictions. 2-Flow behind pipe with flow restrictions. 3-"2D Coning" through a hydraulic fracture from an aquifer. 4-Natural fracture system leading to an aquifer.
C-Treatments with performed Gels are an effective choice. 1-Faults or fractures crossing a deviated or horizontal well. 2-Single fracture causing channeling between wells. 3-Natural fracture system allowing channeling between wells.
D-Difficult problems for which Gel treatments should not be used 1-3D coning. 2-Cusping. 3-Channeling through strata (no fracture), with crossflow.

The most difficult problems facing water treatment shutoff technology are problems listed in the category D, which are 3D coning, cusping and channeling through strata (no fracture), with cross-flow. Where water and gas simultaneously flows from a matricial reservoir into the producing wells, either they are, or not, separated by an impermeable layer (See Fig 1.2).

Gel treatments for the problems in category D (Table 1.2) will be more ineffective, because reducing water permeability will accelerate water to cross-flow to the gas/oil pay-zone if they are not separated by impermeable layer (Seright & Sydansk 2003). Consequently residual gas/oil saturation will increase as the water cross-flow into the pay zone and damages gas/oil path flow into the producing wells. While gel treatments will be successful in matricial reservoirs if there is not cross-flow between the strata the gel has to be only placed into the offending water zone.

On the other hand, most water shutoff treatments which were carried had attempted to reduce water permeability to its minimum value, consequently these treatments resulted low to moderate success. In such application post treatment phenomena are strongly recommended to be occurring, which are increasing water saturation behind the treated area and cross-flowing between the offending water zone and gas/oil pay-zone. To avoid water saturation and cross-flowing problems after the chemical treatment, water permeability should not be reduced severely near the wellbore region. Thus, through this research work a new method is proposed to reduce water permeability gradually from deep in the formation to near the wellbore region. This method is composed of injecting several chemicals sequentially into around the affected wellbore provided each subsequent injected chemical has a higher viscosity.

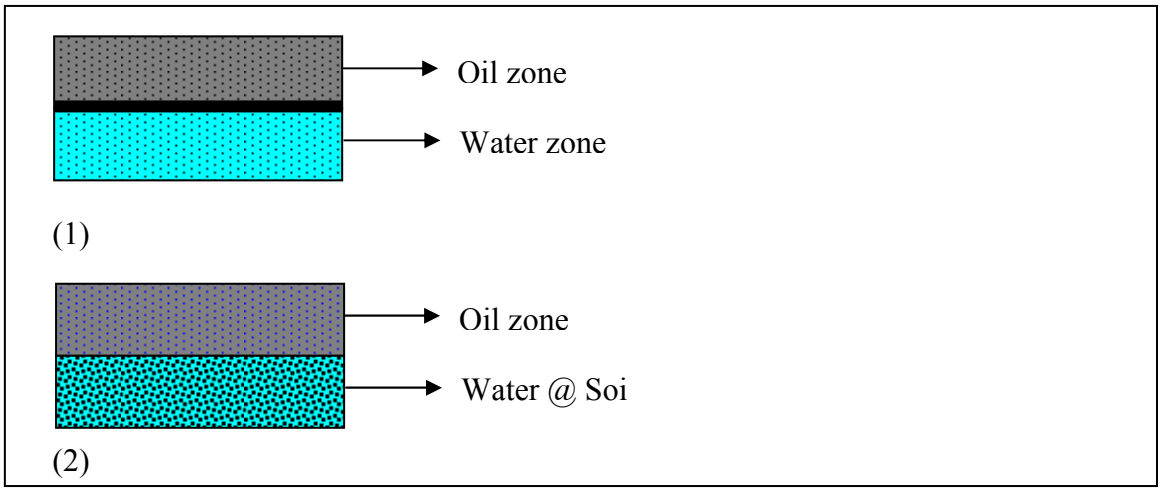


Figure 1.2: (1) Water and oil producing from different zone that separated by impermeable layer such as shale. (2) Water and oil co-produced from different zones that are not separated by impermeable layer.

To achieve a high success rate when treating water production-problem Elphick & Seright (1997) considered the nature of the problem should be identified correctly, and then planning how to battle excess water problems comes next.

However the sources of water production is identified correctly and the following design for selecting candidate chemicals and candidate wells are performed meticulously, the need for a method of field application is still required to enhance post treatment results. Therefore, in most field cases water shutoff treatment by RPM chemicals has shown moderate success (Liang et al 1993; Seright & Sydansk 2003). Although some authors consider the reason for this moderate success is due to poor identification of candidate wells, chemicals and source of water influx (Kume 2003; Seright & Sydansk 2003). Some field treatments, especially in matrix reservoir have been performed after an extensive study while the treatment success was for short periods only (Okasha et al 2001; Zaitoun et al 1991; Zaitoun & Pichery 2001). Thus proposing a method for field application is indeed required to raise the potential of conformance control.

1-2 New proposed technique:

As considered the new method aims to reduce the effect of the inevitable phenomena that usually occur after chemical treatment. These phenomena are increasing water saturation behind the treated area and cross-flowing between the zones (Liang et al 1993). Unlike conventional RPM treatments, for this method water permeability will not reduce to its minimum level or abating completely by placing one super chemical around the affected wellbore region. Figure 1.3 shows the characteristic details of this method that composed of three skins (injected chemicals) into the affected zone. The following is a summary of the proposed chemical zones that would be placed into and around the candidate well regions:

1- L1, Zone-1, it is characterized by low molecular weight, low concentration, high injectivity, low resistance factor (RF), easy partitioning to the rock surface and

reduces water permeability by approximately 20 percent. The chemical candidate for zone-1 should be able to mobilize the trapped oil in the porous medium.

2- **L2**, Zone-2, it is characterized by low to medium molecular weight, relatively high injectivity and reduces water permeability by approximately by 40 percent. The chemical should not face injectivity problem during over-displacing L1.

3- **L3**, Zone-3, it is characterized by high molecular weight, high polymer concentration, and expected to control water flow of at least 60 percent. The chemical should have gelation time long enough to over displace both L1, L2 before being set in the porous medium.

From the outer zone (L1) to near the borehole zone (L3) at each grade (Skin), both residual resistance factor to water (F_{rrw}) and RF increase by a ratio not greater than 2.5. Because the RPM treatment if bullheaded in matricial reservoirs, it is considered risky to drop the relative permeability to water by a ratio greater than 10 (Zaitoun et al 1989). However in our scenario the dropping ratio in total is greater than 10, but it is gradually decreased so it is not too risky to bullhead the chemicals into the anticipated zone without isolation.

Dovan and Hutchins (1994) have advocated a sequential injection method, then Wassmuth et al (2004). Both parties have found that over displacing gelant before set in the near wellbore region by foam or gas has excellent water control performance and concurrently will not hinder the gas flow. Therefore, over displacing L3 near the wellbore by oil, as suggested by this research work, may reduce the effect of chemicals on the oil flows.

Again the purpose of the gradual decrease of water permeability is to reduce water saturation behind the area of treatment, avoiding water cross-flowing and minimizing the affect of chemical on the oil flow. For these reasons, reducing water flow gradually around the wellbore can result in the maintenance of low water production for longer periods after the chemical treatment.

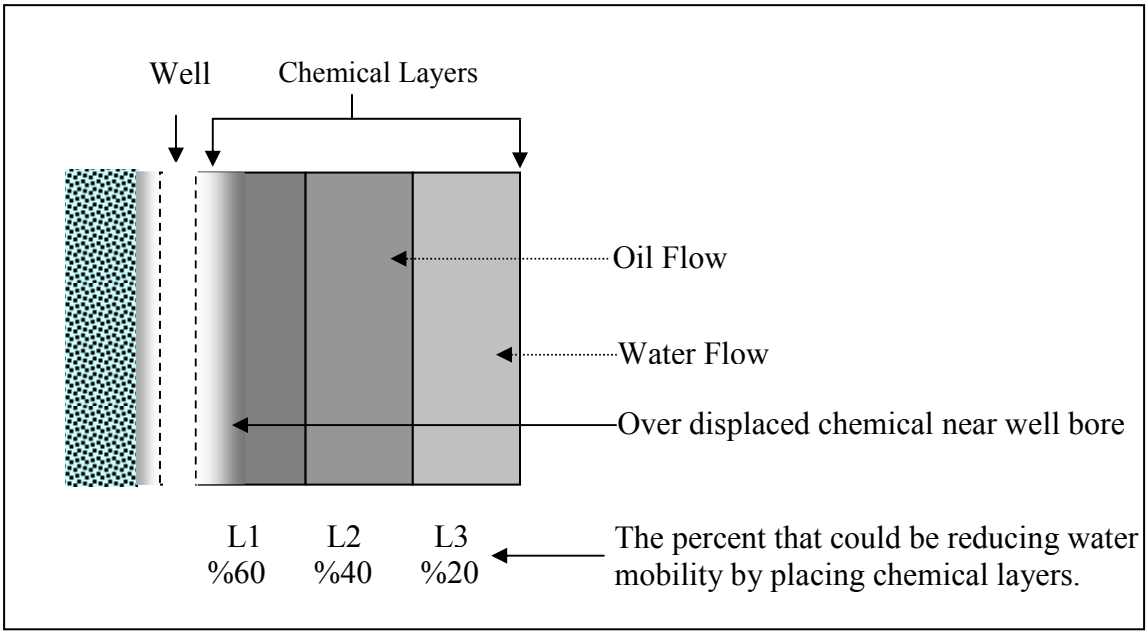


Figure 1.3: Sketch of the new proposed scenario for attacking excessive water production in matricial reservoir by placing several chemical layers around the affected wellbore region.

1-3 Objective and Significance:

The main objective of this research is to evaluate experimentally the effectiveness and viability of newly developed chemicals for water shutoff treatment in matricial reservoirs. Albeit some of these chemicals have significantly demonstrated to selectively reducing water mobility in the laboratory experiments, but in the field contrastingly they revealed low to moderate success especially for healing radial flow. So suggesting a new technique for the field application that leads to the enhanced performance of RPM technology is one of the research tasks.

In addition to the main tasks in this research work there are some lateral tasks that this study is aiming to achieve through the comprehensive core-flooding experiments performed on different chemicals in both Berea and reservoir core plugs.

The subsequent aims in this project are:

- Screen and evaluation of RPMs (effects of multi-component systems)
- Evaluate and select lower-cost/higher performance RPM's
- Investigate how they work
- Develop RPM transport models
- Evaluate the oil/gas mobility improvements for reservoirs, and
- Evaluate the influence of experimental conditions, such as permeability alteration, pressure, temperature, pH, brine salinity, saturation distribution, and flow rate.

The significance of this research will have the following advantages:

- Economically; reduction in excess water production with major economic benefits for operators. Worldwide costs are US $40 billion a year.
- Environmentally; preventing water production in situ, especially at offshore fields. This will reduce the impact of water handling at the surface.
- Physically; enhancing well function, preventing fine influx, reversing pressure decline and increasing sweep efficiency
- Contribute to future research work seeking the same aim.

1-4 Thesis outline:

The details of the seven chapters are:

Chapter One: Introduction into the topic and the impact of excessive water production both economically and physically on the reservoir performance are presented. The identification of the problems and the sources that cause excessive water production are discussed, together with offering an optimized solution for each different sources of water production. Moreover the new method for injecting chemicals sequentially is discussed. Finally the advantages of this research are also briefly presented.

Chapter Two: Includes an intense literature review on water abatement and the review of the rules in selecting candidate wells, chemicals and the field processes.

Chapter Three: Presents the result of the core flooding experiment conducted on Wanaea core plugs from Woodside. In this chapter four newly developed chemicals have been tested to find their effectiveness to reduce water permeability under Wanaea reservoir conditions. The chemical were prepared by WaterWeb, Reltreat, AquaCon, and Curtin University WRF. The Curtin University sample was prepared by Professor Amin. The rheology of the chemicals and their compatibility to the reservoir condition such as brine, temperature, pH, and absorption with rock surfaces had been intensely studied by their providers.

Chapter Four: This chapter is set to the rheology study and screening of the chemicals that are prepared in the WRF laboratory. There were three additional chemicals, each individually tested in Berea sandstone to examine chemical strength under various reservoir conditions. As a result of these tests the effects of permeability alteration, flow rate, BP pressure, brine salinity, temperature, and rock

porosity/permeability have been examined on the chemical durability inside Berea plugs. These chemicals are composed of different gel with differing concentrations.

Chapter five: Presents the obtained results from linear core-flooding test that are carried out on the prepared chemicals in WRF laboratory. The aim was to assess their effectiveness to reduce water permeability selectively under different reservoir conditions. Furthermore the results of two phase flow tests are presented with their consequence on chemical abatement. The results of two phase flow tests recommend; over-displacing chemicals near the wellbore region after the treatment by oil will be crucial factor to enhance oil mobility after the treatment.

Chapter six: Is a display of the results achieved from injecting chemicals sequentially test in Berea sandstone. As well describing the basis on how the chemicals were selected for this test. It also includes the comparison between the results from this method tests and the results obtained from experiments when these chemicals have been injected individually. The results demonstrate that the new technique of injecting chemicals sequentially, to decrease water permeability, is a more efficient method than injecting only one super chemical.

Chapter seven: This Chapter provides the conclusions from this research work as well as the recommendation for improving water shutoff technology by applying sequential injection methods.

Chapter 2

Literature review

2-1 Mechanisms of water influx:

Most reservoirs that are subjected to an active aquifer will experience water encroachment after they have been producing for sometime (Sidiq et al 2007).When the mechanism of water influx into the wells is identified, mitigating excess water production can be easily achieved. Water can be produced either as the result of mechanical failure in the wells completion (such as casing and pipe leaking, slotting at water interval, bad gravel packing, etc) and naturally occurs as the result of pressure decline through out the reservoir. It produces to the well typically from fractures, channel (heterogeneous medium) or matrix flow (homogenous medium).

Treating excess water problems that occur as the result of mechanical failure can be overcome with ease and the conventional mechanical methods would be an alternative choice (Table 1.2). On the other hand, the water that is produced as the consequence of field maturity, chemical abatement to control water in situ would be an effective choices rather than mechanical means. The mechanisms by which excessive water from reservoir produces into the wells mainly depend on:

- Reservoir condition (Pressure and temperature),
- Petrophysical properties (Porosity, permeability, mineral, etc),
- Wettability,
- Rock type (heterogeneous or homogeneous), and
- Aquifer condition (salinity, geometry, etc)

Therefore, different chemicals have been formulated for water shutoff treatments depending on the factors that affected the mechanism of water production (Faber et al 1998; Seright 1993).

2-1-1 Flow from homogeneous medium:

In a reservoir where the flow is from matrix rock lack of fractures, high streak permeable layers, faults, and joints, water encroachment into the reservoir depends on pressure decline through out the reservoir. As the water influxes into a volume of rock, water displacement to hydrocarbon will be incomplete, consequently residual oil/gas saturation increases (Sidiq et al 2007). Water invades a pore and pore's throat, causing capillary pressure and relative permeability effects to stop the flow of gas and allow only water to pass through the rock volume (Holtz 2002).

Usually homogeneous rocks are characterized by a low ratio of permeability contrast (vertical permeability to horizontal permeability), and a lack of an impermeable barrier (shale or other) between water and hydrocarbon zones. The fluid flow in this type of reservoirs is considered to be radial flow around the well. One simple method used for diagnosing this type of flow from linear, it to use the Darcy equation for radial flow (Seright & Liang1994), as below:

$$\frac{q}{\Delta p} = \sum kh\left[141.2\mu \ln\left(\frac{r_e}{r_w}\right)\right] \qquad (1)$$

where q is the flow rate, Δp is the pressure difference, K is the permeability, h is the height of pay zone, μ is the viscosity of the produced fluid, r_e drainage radius, and r_w is the wellbore radius.

If the actual injectivity/productivity for a well (left side of Eq.1, q/Δp in BPD/psi) is less than or equal to the calculated injectivity/productivity with the Darcy equation for radial flow (right side of the equation), radial flow is expected.

Mostly all 3D coning, cusping, and channeling corresponds with radial flow types. Several authors (Kume 2003; Seright & Sydansk 2003) have stated that performing chemical water abatement in matrix reservoirs that are suffering from radial flow will not be an appropriate treatment for controlling water production selectively. This is because the injected chemical not only reduces water flow but also impedes hydrocarbon production as well (Kume 2003). The chemical cannot stop water flow deep into the formation but it is only set to hinder near the wellbore to reduce water flow. As a consequence water saturation increases and subsequently cross-flow happens.

In contrast, it could be a suitable alternative to be used for reducing excessive water production in matrix reservoirs provided that the water and the hydrocarbon zones are separated by an impermeable layer. As well, in multi-well development fields, having high drainage from offset wells, chemical abatement could be successful as there is an alternative path for water production existing at offset wells.

2-1-2 Flow from Heterogeneous medium:

In a reservoir where the water paths into the producing wells are different from the paths that gas/oil flowing into the production wells is considered as heterogeneous medium. The path could be the result of natural fractures, geological faults, joints, high streak permeable layer or channels. The affinity of water to channel through a gas reservoir to the producing wells has been one of the most serious problems associated with gas production throughout the world (Zaitoun & Kohler 1989, p 56).

The fluid flow from these types of rock is generally considered to be linear flow around the wellbore. Seright (1988) found that the tools that have been used for compromising linear flow problems must fundamentally be different from those used to solve radial flow problems in matrix reservoir.

The easiest methods for identifying linear flow from radial is modifying equation-1, basically when the left side of Eq.1 is five or more times greater than the right side the well probably suffers from linear flow, i.e.:

$$\frac{q}{\Delta p} >> \sum kh\left[141.2\mu \ln\left(\frac{r_e}{r_w}\right)\right] \qquad (2)$$

However the above equations are not always being a discerning method for distinguishing radial and linear flow. Nevertheless they frequently do provide a definitive indication of the flow geometry near the wellbore, because the calculations are easily performed with data often at hand (Seright & Sydansk 2003).

Often a variety of chemicals have been used to mitigate excess water production in heterogeneous mediums. The most successful applications in the field were carried out in Western Kansas and Wyomin fields, where they suffered from linear flow (Seright 1995; 2003). One of the most serious problems facing chemical treatment with linear flow is washing-out the gel from the fracture after the treated wells allow to production (Moffit 1993; Sydansk & Moore 1992).

2-1-3 Methods used for diagnosing water production:

Identification of the mechanisms by which water arrives into the producing wells should be performed correctly before designing any water shutoff treatment. Probably 30 methods are available for diagnosing different types of water production problems (Seright & Sydansk 2003). The presence of too many methods raises the degree of uncertainty among the operators to decide which method is cost effective for diagnosing water problems. Therefore in many, perhaps most, cases the identification of the source of the problems had not been performed correctly which resulted in less than 50 % success rate (Pappas et al 1996).

Furthermore, due to variety of methods, including time and cost, most operators do not agree to perform complete diagnose for identifying the source of water production. Moreover, the common belief among most of the engineers that there is only one method that can solve all water production problems or there is only one type of water production exist such as water coning has inspired operators to not perform further diagnosis on the affected wells (Seright & Sydansk 2003). Consequently this has resulted in low to moderate success rate recorded in the field by applying chemical treatment.

The following are reviews of some common and easy methods which have been used for the identification of water production problems:

A- Problem caused by leaks or flow behind the pipe:

These problems are assigned as the easy problems in the view of excess water production and could be solved before the more difficult problems. The most common techniques used to diagnose these types of water problems are:

- Temperature survey,
- Flow profiling tools (e.g. radiotracer flow logs, spinner surveys, etc),
- Cement bond logs,
- Borehole televiewers, and
- Noise log.

B- Problem caused by fractures:

Several methods can be used to determine if fractures are the source of the water problem. They include:

- Core and log analyses,
- Test pressure transient analyses, and
- Interwell tracer studies.

As expected the flow from fracture or fracture like features are always associated with linear pattern. Thus, simply by using the first two equations, Eq 1 & 2, which mentioned in the preceded paragraphs, can presume that the nature of flow in the affected wells is either suffering from linear flow or from radial flow.

Fracture's volume, permeability, and orientation can be defined by pressure transient analyses (Aguilar 1980, p.125). Inter-well tracer studies have been used to provide fracture characterizations in reservoirs, especially for use in judging the applicability of gel treatments to reduce channeling (Wangner 1977, p1410).

C- Problem caused by Matrix flow:

Matrix flow is frequently associated with cross flowing between the strata, if the cross flowing exists the following methods are used for identification:

- Pressure test between the zones,
- Various logs for determining fluid saturation, permeability, porosity and lithology,
- Injectivity and production profiles, and
- Simulations.

The straightforward method for defining cross flow associated with matrix flow is a pressure test between the zones. This test is performed by placing a packer between the expected zones, then raising the pressure against one of the zones if the pressure is maintained during the pressurization it reveals the fact that cross flowing does not exist, and vice verse.

Another method for determining matrix flow is by plots of WOR (water oil ratio) verses time. It can provide a valuable indication of when an excess-water problem develops (Chan 1995). The diagnostic plots (WOR or WOR-derivative verses time) should not be applied alone to identify the mechanism of excessive water production and problems (Seright & Sydansk 2003). It is possible to distinguish whether a

production well is experiencing premature water breakthrough that is caused by water coning (matrix flow) or channeling through high permeability layers (linear flow) (Chan 1995). According to this method, gradually increasing WOR curves with negative derivative slopes are unique to coning problems (See Fig 2.1), and rapidly increasing WOR curves with positive derivative slopes area indicative of a channeling problem (See Fig 2.2).

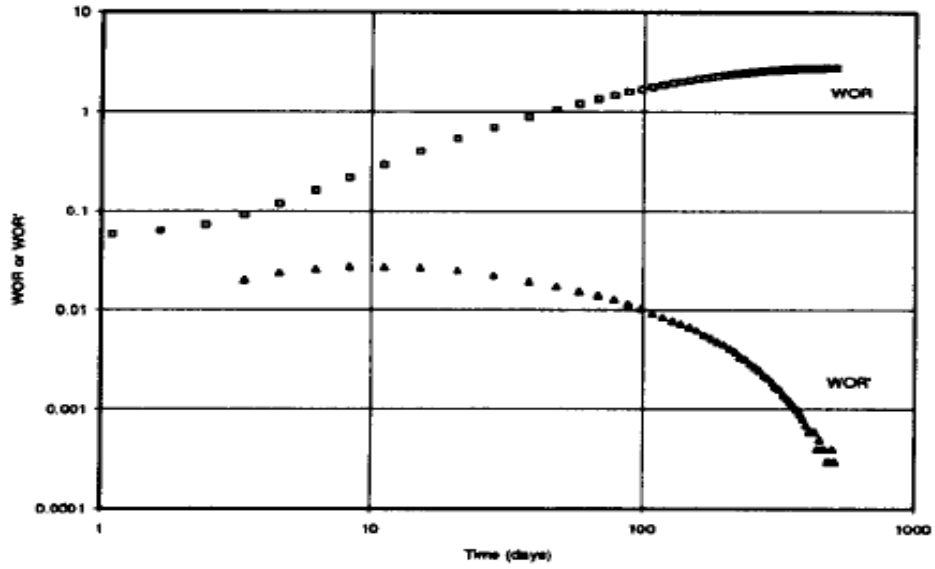


Figure 2.1: Bottom- water coning WOR and WOR derivatives. After Chan (1995).

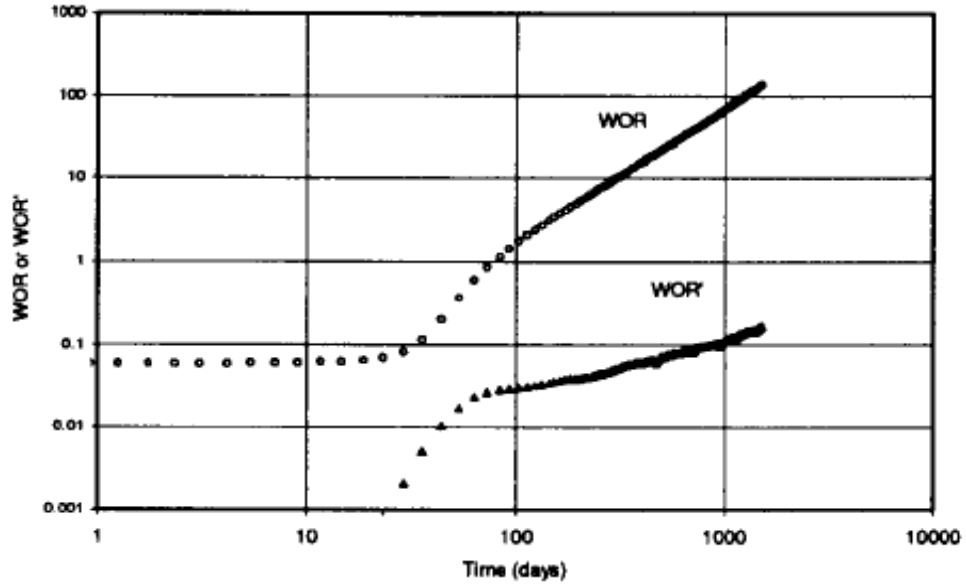


Figure 2.2: Multi-layer channeling WOR and WOR derivatives. After Chan (1995).

D- Problem is caused by high permeability streaks:

To presume the location of high permeability streak from the data that is already in hand the following steps are required:

1. Plotting air permeability and porosity versus depth of the affected wells reveals the depth that high permeability streak can be anticipated.

2. Calculating hydraulic properties of the reservoir are significant to recognize reservoir zonation. In other words, the hydraulic unit is a statistical representation of reservoir zonation and quality (Okasha et al 2001).

The concept is defined by equations 1 to 4:

$$RQI = 0.0314\sqrt{\frac{ka}{\phi}} \qquad (3)$$

Where,

RQI = reservoir quality index, μm

Ka = permeability to air (mD)

ϕ = porosity, volume fraction

The normalized porosity index (*NPI*) was obtained using equation 4:

$$NPI = \frac{\phi}{1-\phi} \qquad (4)$$

Both *RQI* and *NPI* functions have used to measure the flow character of a reservoir Using *RQI* and *NPI*, a flow zone indicator (*FZI*) is defined as:

$$FZI = \frac{NPI}{RQI} \qquad (5)$$

When *RQI* values are plotted on a normalized cumulative basis with depth, deviation in slope trend represents various reservoir rocks. The evaluation is based on observing changes in slope trends, gentle slope indicates high reservoir quality (high permeability zone) while steep slope annotations to poor reservoir quality (low permeability zone). (See Fig 2.3)

$$X_i = \frac{\sum_{X=I}^{i} \sqrt{\frac{k_i}{\phi_i}}}{\sum_{X=I}^{n} \sqrt{\frac{k_i}{\phi_i}}} \qquad (6)$$

Where,

XI = normalized-cumulative sum of RQI

n = total number of data points

i = number of data points at sequential steps of calculation

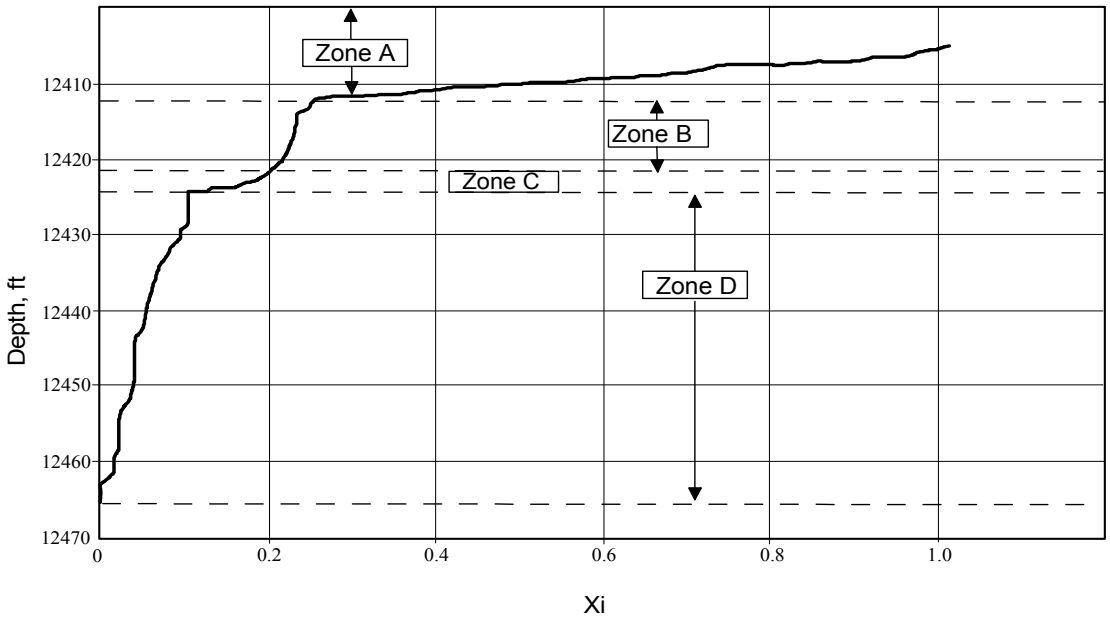


Figure 2.3: Cumulative reservoir quality index (Xi) verses depth. Zones A and C expected to be high permeable zone as they have gentle slope. After Okasha et al (2001).

2-2 Factors affecting fluid flow in reservoir:

In practical situations it is important to estimate in advance, before the treatment, the factors that have been robustly affect on fluids flow in the mixed wet reservoir. In mixed wet reservoir, relative permeability and residual water/gas or oil saturation control the fluid flow in the porous medium. Therefore reviewing these factors is crucial for designing water abatement chemicals technique. Because placing RPM into the reservoir rocks will affect directly on both relative permeability and phase saturation ratio of the fluids resided in the reservoir porous medium (Chan et al 1997; Holtz 2002).

The factors are:

1. How the wetting fluid gets in (either forced or spontaneous imbibition),
2. Type of wetting fluid,
3. Rate of imbibitions,
4. Rock type (lithology, pore type, grain size and sorting),
5. Wettability and interfacial tensions,
6. Temperature and pressure conditions, and
7. Petrophysical properties (porosity, permeability, initial gas saturation).

For decades the above factors and their effects on relative permeability and residual gas/oil saturation in reservoir rock have been studied in detail by many researchers. However the effects of the individual factors on fluid flow under a certain reservoir condition require a through study. Briefly, their effects on both relative permeability and residual gas saturation can be found elsewhere (Ahmad 2001; Chan et al 1997; Holtz 2002; Mulyadi 2002).

2-3 Review of RPM

2-3-1 Introduction:

The conventional chemical methods often represent an essential and economic alternative technique over mechanical isolation provided the water and gas zones are identified correctly and the chemical systems are formulated properly prior to their placement into the candidate wells.

Polymer gel systems have emerged as one of the most effective conformance solutions for controlling water production in situ over the last decade (Vasquez 2004). For almost three decades many polymer systems have been investigated in laboratories to estimate their potential use under different reservoir rocks and different reservoir conditions.

The common polymeric gel systems reported to selectively reduce water production are polyacrylamides, partially hydrolyzed polyacrylamides (PHPA), xanthan gum, carboxymethylcellulose, resorcinol formaldehyde, Cr (III) acetate-HPAM, furfural-alcohol, acrylic/epoxy resins, colloidal silica gels, and block copolymers (Dovan & Hutchins 1994; Faber et al 1998; Seright 1988; 1993; 1995; 2003; Seright & Liang 1994; Sidiq et al 2007; Sydansk & Moore 1992). In order to obtain high performance control they are some times cross-linked either with metallic (Cr, Al, Zr) or with organic cross-linkers. Organic cross-linker gel systems are more stable under high temperature, with field results showing high success in reducing water production (Hardy et al 1999). Usually formaldehyde is added into the bulk composition of the gel system to minimize the effect of polymer degradation by the bacterial activity if the aqueous phase of the polymer was fresh water.

Multivalent polymer, amphoteric polymers and micro-gel systems are the versatile polymer systems for a matrix reservoir as they cover a wide range of permeability (Botermans et al 2001). They are characterized by high water soluble polymer, high hydrophilic, and easily partitioned onto the rock surface and into the water phase.

Many polymer systems used to control water conductivity in fractures, joints, and high permeability layers are formulated similarly to polymer systems that have been used for mitigating matrix flow. The only difference to be noted is the polymer concentration in the aqueous phases. The polymer concentrations have been used for reducing water production from high permeable zones ranged approximately 1-5 % (Okasha et al 2001; Seright 1995).

2-3-2 Polymer mechanism:

Polymer adsorption onto the reservoir rock surfaces induces a selective reduction of the relative permeability to water with regard to the relative permeability to oil or to gas. The mechanism of polymer adsorption and partitioning in porous medium is still controversial. There are two main hypotheses on how polymer works to reduce water permeability selectively in pore scale:

- First - fluid partitioning theory

The fluid partitioning theory states that gas/oil and water, inside the porous medium, flow as segregated paths and the gel tends to hinder water paths, thus water mobility is reduced preferentially (Liang et al 1995; Liang & Seright 1997). (See Fig 2.4a)

- Second - wall effects theory

After injecting the gel in to the porous medium a thin layer or film of gel covers the pore walls and pore throat causing a reduction in effective pore size. Water mobility will reduce by increasing the film thickness as the gel film retains more water into its structure during water flow in the pore channels. Nevertheless gas/oil mobility remains approximately as the same rate by squeezing the film when the gas/oil flows through the pore channel (Mennella et al 1998). (See Fig 2.4b)

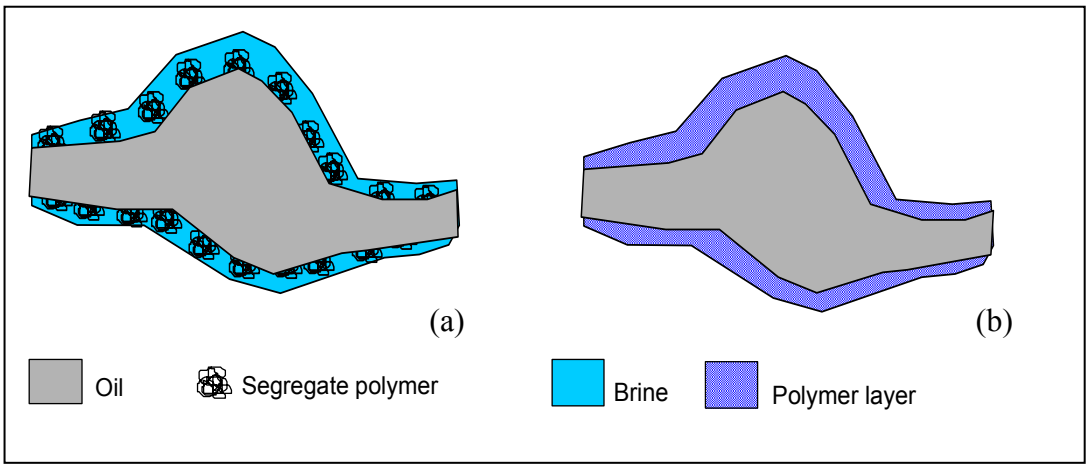


Figure 2.4: Schematic representation of polymers effect on how reducing the size of the pore space. (a) Fluid portioning theory (b) Wall effect theory.

2-3-3 Gel-rock interaction mechanism:

The mechanism that controls the dispersing gel onto the rock surface is crucial when selecting the gel for water shutoff treatment. Polymers should be selected according to their ability to display strong attractive interactions with the rock surface in order to maximize adsorption and layer stability (*Mennella et al 1998).

The two types of rock-polymer interaction are:

- Dispersion interactions (London, van-Der-Waals); which are generally attractive and are controlled by polymer structure and molecular weight, and

- Electrostatic interactions between charge groups present at the polymer/brine and rock/brine interfaces. In particular, electrostatic interactions has important role in the adsorption process, as they can be an attractive or repulsive force (Chiappa et al 1998; Mennella et al 1997).

Moreover, in the porous medium when gel is placed, many factors will affect the electrostatic interactions process between the rock surface and the spread gel. They can be classified as either chemical or physical factors. In other word these factors are responsible for controlling the polymer adsorption onto the reservoir rock surface. In addition they have great influence on the sturdiness and effectiveness of the gel during and after propagation in the formation pore spaces.

2-3-4 Chemical and Physical Factors:

1. Effect of ionic strength and composition:

Chiappa et al (1998) and **Mennella et al (1998) have studied the effect of ionic strength and brine composition on the adsorption process of gel onto the surface of siliceous and reservoir sandstone. In their experiment, a static adsorption test, they found positive charge polymers (CAT) are more attractive than negative or neutral charged polymer (PAM and HAMP) to be absorbed by the grains of sandstone. The results in Figures 2.5a and b show how electrostatic interactions play a dominant role in the adsorption onto surfaces of siliceous and reservoir sandstone.

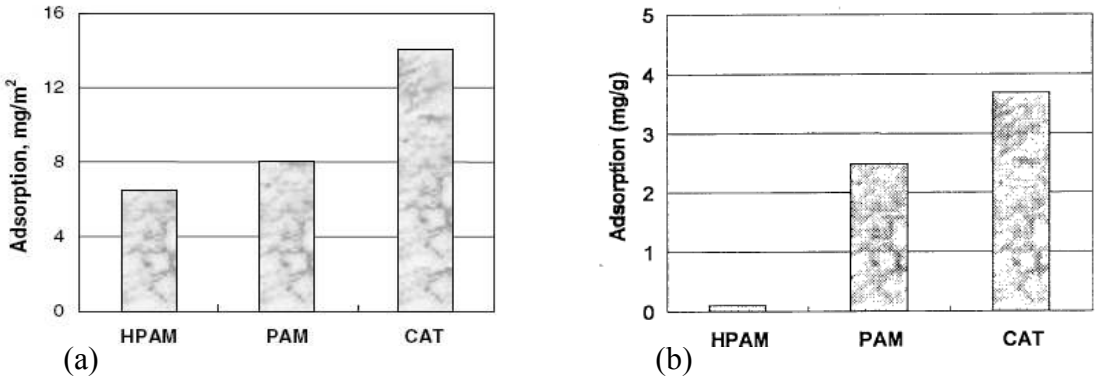
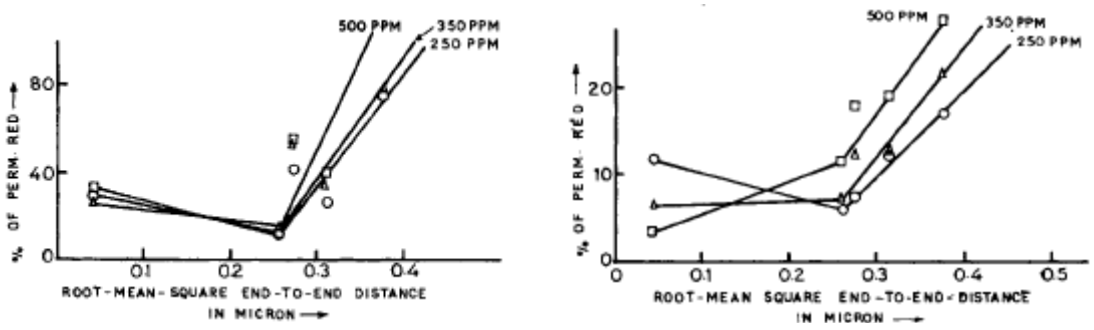


Figure 2.5: Equilibrium adsorption of polyacrylamides of comparable molecular weight (PAM and HPAM – 5 million, CAT – 2 million) and different charge (negative – HPAM, neutral – PAM, positive – CAT) onto pure quartzite (a), and gas reservoir sand (b). Polymer solutions (2000 ppm) were prepared in 2 % KCl brine. After Chiappa et al (1998).

2. Effect of molecular weight and concentration:

Baijal and Dey (1982) have studied the role of polymer molecular weight and concentration on the flow propagation inside a porous media. Five different polymers were investigated in their study, these being Polyacrylamide, Separan MG-200, Pusher 700, Pusher 500, and Polyacrylic acid.

With increasing molecular weight and concentration the permeability of the medium decreases noticeably, thus polymer adsorption increase with increasing both molecular weight and concentration. Furthermore, they presumed under a certain molecular conditions, polymers molecule can be deformed easily in dynamic conditions, hence permitting greater interaction with the surface of the porous materials of the media. (See Fig 2.6)



(a) (b)

Figure 2.6: Permeability reduction vs. polymer molecular diameter in (-100+ 200) mesh, (a) fresh sand pack, and (b) pretreated sand pack. After Baijal and Dey (1982).

3. The role of clay content:

Because clays are characterized by high surface area and negatively charged, physically it will be attractive for polymers that have positive charge (CAT). Mennala et al (1997) in an experiment found that CAT polymer adsorption increases more than PAM and HAMP with increasing clay mineral in the structure of the sandstone. (See Fig 2.7)

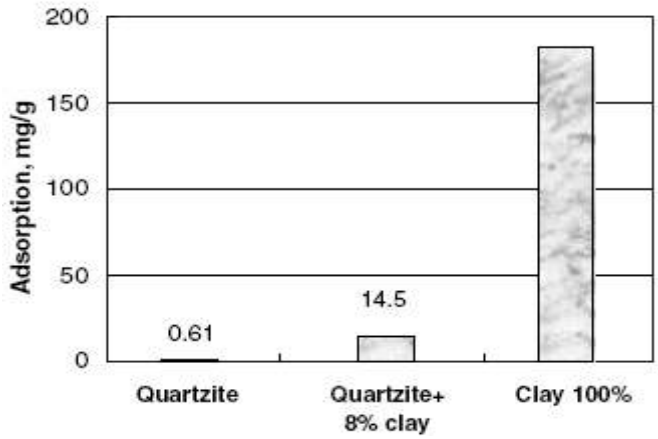


Figure 2.7: Equilibrium adsorption of CAT onto siliceous sands with different clay content. Data is plotted in mg of polymer adsorbed per gram of sand, because the grain-size distribution and, therefore, the surface area of clay minerals were unknown. Polymer solutions (2000 ppm) were prepared in 2 % KCl brine. After Mennella et al (1997).

4. The role of Wettability:

Sandstone oil reservoirs are presumed to be mixed-wet reservoir, Salathiel (1973) postulated a mechanism by which a reservoir could become mixed-wet as a result of crude oil migration. Therefore adsorption test of polymer on clean sandstone could be misleading.

In a study Chiappa et al (1998) established that an oil-wet medium has a crucial impact on the adsorption of differently charged polymers onto the rock surface. They used both PAM and CAT polymers in their tests and found in the presence of oil that polymer absorption remarkably decreased. However CAT polymer adsorption is still significant if compared to its adsorption in clean sandstone. (See Fig 2.8).

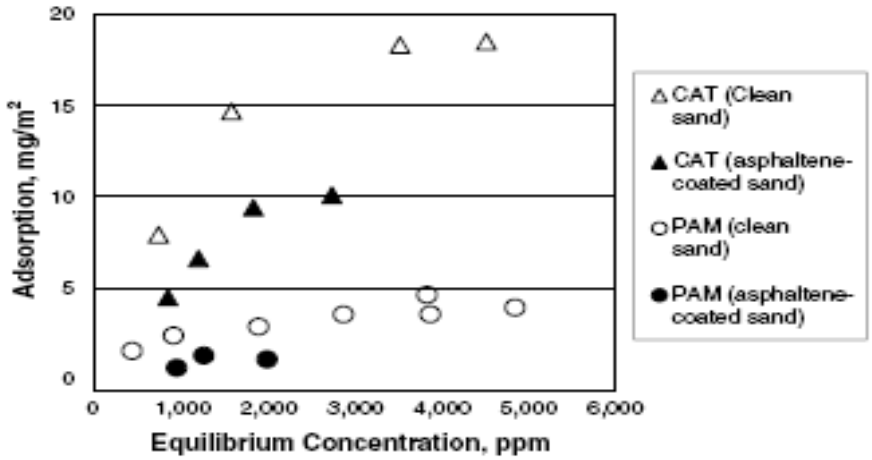


Figure 2.8: Adsorption of isotherms of polymers CAT and PAM onto oil-wet quartzite. The isotherms of the same polymers on clean quartzite are also plotted for comparison. After Chiappa et al (1998).

5. The role of brine salinity and composition:

**Mennella et al (1998) studied the effect of brine concentration, KCl 2000 ppm, on different (electron charge) polymer (PAM, HAPAM, and CAT). The result of their experiment indicated that although the increase in ionic strength causes a slight decrease in the adsorption of CAT (presumably because of electrostatic screening) the trend in polymer adsorption vs. polymer charge is maintained. (See Fig 2.9a)

They noticed a very different behavior when a divalent cation is added to the brine composition. The adsorption of PAM and HPAM (which show very similar trends) is greatly enhanced, attaining values greater than CAT at concentrations of $CaCl_2$ over 6 % (See Fig 2.9b). The increase in absorption by rock grains interpreted to be as the result of the ionic attraction (Bridging) between the positive charge Ca^{2+} ions and negative charge of PAM and HPAM polymers.

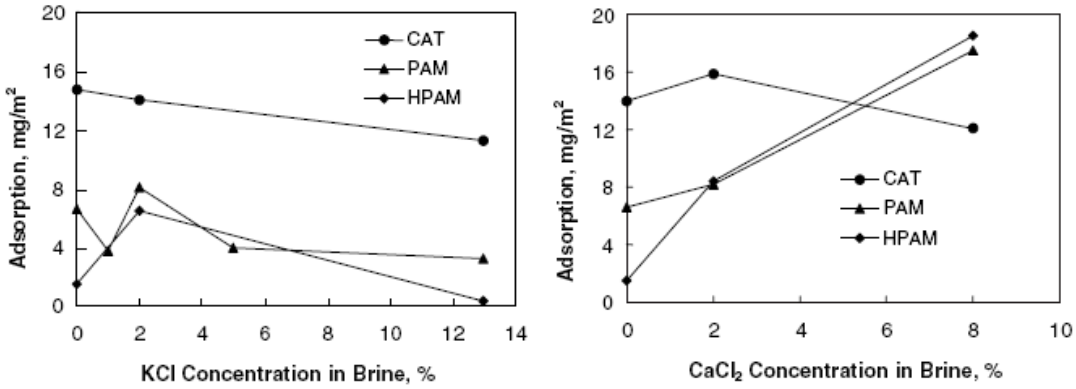


Figure 2.9: Adsorption of polymers of different charge onto quartzite from brines with different ionic strength. The graphs show the effect of (a) monovalent ion (K^+), and (b) divalent ion (Ca^{2+}) on Polymer adsorption. After **Mennella et al (1998).

2-4 Rules and Guidelines for selecting candidate wells and chemicals:

Whenever the sources of water influx into the reservoir and the factors that are affecting the gel propagation in the porous medium are identified, selecting candidate wells and chemicals becomes an issue. Zaitoun et al (1989), **Mennella et al (1998) and Chou et al (1994) derived some guidelines that can be used for discerning candidate wells and chemicals. The guidelines depend on the laboratories and field application results that are reviewed by these authors. The next paragraphs contain the recommendations on how to select appropriate chemicals for affected wells.

2-4-1 Selecting candidate wells:

1-Producer wells:

- Being isolated from other producer's problems, or having no offset injectors. In other words, showing low correlation with offset injectors.
- Having high fluid level in the well, which prevents production from lower-pressure, oil bearing zones.

2-Injector wells:

- Offset injectors are good candidates if having a high correlation coefficient with their problem producer.
- The correlation coefficients should be calculated over an appropriate time frame, in order not to reflect (only) the overall trend of rising production due to water injection.

3-General points of candidates:

- Having near-wellbore virgin oil layers are good candidates (e.g young wells suffer from sudden water influx).

- In heterogeneous reservoirs, matrix formations, without cross-flow between the layers, having high permeability contrast, and one or more layers that are still saturated with hydrocarbons are also good candidates.

- In homogeneous reservoir (e.g. water coning) where water is mobile in all productive layers, the benefits from an RPM treatment can be of limited duration because it may cause significant reductions in bottom hole pressure.

- In high permeability formations (K > 2D) it can be difficult to achieve high permeability reductions simply by polymer adsorption.

- However having clay minerals in the reservoir formation increases polymer adsorption rate, but due to the heterogeneous distribution of the clay mineral it is possible that the polymer will preferentially adsorb in the clay-rich portions of the rock.

2-4-2 Selecting candidate chemicals:

- Cationic polymers are particularly recommended for applications in siliceous formations as well as on reservoir sandstone.

- Polymer adsorption tests provide a useful preliminary comparative assessment of the performance of different systems.

- The optimal molecular weight has to be defined considering principally the injectivity properties of the polymer solution. In general the choice is a compromise between the following requirements:
    - Increase adsorption (then higher molecular weights are preferred).
    - Limit mechanical plugging during injection (then lower molecular weights are preferred).

- The presence of divalent cations in the polymer solution can substantially increase the adsorption of negatively charged polyacrylamides (HPAM).

- The presence of crude-oil can substantially reduce the polymer tendency to adsorb onto the rock surface. Therefore, in crude-oil reservoirs, direct extrapolation of results obtained with clean sand and model oils can be misleading.

Chapter 3

Wanaea Core Flood Tests

3-1 Introduction:

The Wanaea oil field is located in some 80m of water approximately situated 100km offshore North Western Australia (Walters 1996). It composes of an anticline with minor crestal faulting, the dimension of the structure is 3.5 km wide and 11 km long at the hydrocarbon-water contact. The producer unit is predominantly composed of sandstone sequence of Tithonian age (Winterhalder & Hann 1991). In recent years some of Wanaea production wells experienced high water cut therefore chemical abatement is proposed with the aim to reduce water production selectively. For this purpose, four newly developed RPM chemicals are tested with core plugs taken from Unit II of well Wanaea-3 (core depth 2832.00 to 2844.50 m). The laboratory experiments carried out were linear core-flooding, throughput tests. The sequences and the steps of the test producers are shown in table 3.2. For each plugs a suitable chemical has been prepared according to the information already in hand about Wanaea reservoir conditions. Laboratory experiments conducted on the four core plugs determined the core plugs air permeability ranging from 158 to 334 md and porosities from 16.4 to 19.9 %, while absolute water permeability at reservoir condition ranging from 77.9-190 md.

Furthermore the experiments conducted on the Wanaea core plugs have two main objectives which are:

- The potential use of these chemicals under Wanaea reservoir conditions to reduce excessive water production.

- The utility of the chemicals to be applied for the new method tests (injecting chemicals sequentially).

3-2 Test method:

To evaluate certain chemical applicability for a specific field application in the laboratory, most of the researchers (Dovan & Hutchins 1994; Faber et al 1998; Okasha et al 2001; Zaitoun et al 1991; Zaitoun & Pichary 2001; Seright 1988; 1993; 1995; 2003; Holtz 2002; Seright & Liang 1994; Sidiq et al 2007) had performed conventional throughput core-flooding tests. This test method provides an indication to presume a chemicals' validity under reservoir condition, because it simulates the actual reservoir condition during the test. The test conditions were applied on the core plugs have:

- Temperature of 110^0 C,
- Overburden pressure of 2250 psi, and
- Flow rate of 2 cc/min,

These test conditions are maintained throughout the test sequences for the testing each chemical.

3-2-1 Source of water influx in Wanaea reservoir:

Without precise diagnostics of the water source, the results from laboratory experiments may be misleading in combating excess water production. Unfortunately the majority of water abatement by RPM in the field has shown moderate success (Seright & Sydansk 2003). In the case of the Wanaea reservoir the identification of the water source and its nature was carried out by Woodside Ltd, the operator of the field. Depending on the results, both water and oil can be flowing into the wells simultaneously through matrix medium, the depth of the affected zones ranging from 2832.00 to 2844.50 m (See Fig 3.1). After determining the water source, a throughput test sequence is designed in a way to optimize test costs and at the same time the results can reveal precisely the reservoir condition. Accordingly one phase flow tests are selected in this project.

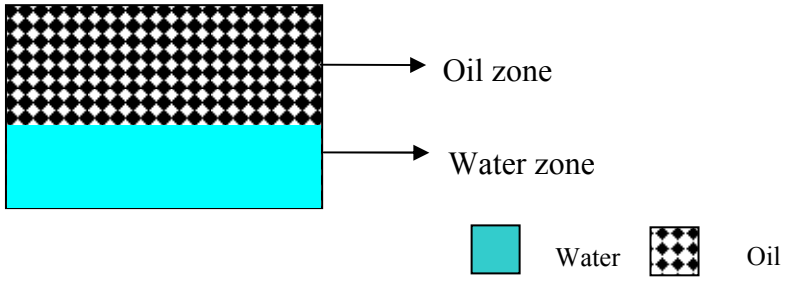


Figure 3.1: Sketch section of anticipated water source in Wanaea reservoir.

3-2-2 Brine Preparation:

The simulated brine used in the tests was prepared by dissolving 24 grams of 80 % NaCl and, 20 % KC in each liter of distilled water. The resulting 24000mg/l salinity approximated the salinity of the Wanaea formation brine.

3-2-3 Chemical preparation:

The four recently developed chemicals used in this study were prepared by WaterWeb, Reltreat, AquaCon, and Curtin University (WRF). The Curtin University sample was prepared by Professor Amin. The rheology of the chemicals and their compatibility to the reservoir condition such as brine, temperature, pH, and absorption with rock surface had been intensely studied by their providers. Due to this prior testing no further tests were carried out on these chemicals to verify their stability under Wanaea reservoir conditions. The main purpose for this study is to experimentally verify the applicability of these chemicals to be placed in the Wanaea reservoir to selectively reducing water production.

3-2-4 Core Plug preparation and testing:

The core plugs used in the tests were reservoir cores from Wanaea reservoir. Laboratory analysis carried out by this researcher with the aid of technical staffs at Core-laboratory. The tests indicated that the air permeability of the core plugs ranged from 181 to 334 mD and their porosity varied from 16.4 to 19.9 %. The core plugs were 7.34cm in length and nearly 3.14cm in diameter. The properties and depth of the tested cores are listed in Table 3.1. The selected core plugs were cleaned by flushing the sample with toluene until the outlet fluid demonstrates clean toluene.

Table 3.1: Basic properties of the core samples tested.

SAMPLE NO.	Depth (M)	TREATMENT CHEMICAL	Length (Cm)	Area (Cm^2)	PV (Cm^3)	GD (g/cm^3)	POROSITY (%)	Ka (md)
27	2839.1	Waterweb	7.42	11.4	16.79	2.65	19.9	334
13	2834.9	AquaCon	7.43	11.4	15.86	2.67	18.5	291
37	2842.1	Reltreat	7.42	11.4	14.15	2.69	16.4	181
23	2837.9	RA	6.59	11.34	13.35	2.66	17.5	158
11	2834.3	Control Sample	7.41	11.4	14.81	2.68	18.5	260

The cores were evacuated and pressure saturated with the simulated formation brine and loaded individually into core holders for testing on a sequential basis. Each loaded sample was then placed in an air-bath and the temperature increased to the Wanaea reservoir representative temperature of 110 ^{0}C. A confining pressure of 3250 psi and a pore pressure of 1000 psi were maintained throughout the analytical sequences (See Fig 3.2)

The core flood tests followed the sequence of steps as shown in Table 3.2, with some variation with respect to chemical injection as some of the chemicals required a pre-flush before the main chemical treatment.

Each of the four samples was tested with a different RPM (Waterweb, Aquacon, Reltreat, and RAC) while a fifth sample was used as a control. This control sample was subjected to the same sequence of testing (comprising multiple cycles of oil and water flow) as the other four samples except that there was no chemical treatment. Results from the control sample were used to determine whether or not variations in oil and/or water permeability were simply a result of hysteresis effects created by changes in fluids saturation distribution in the pore spaces during the multiple flow cycles.

Table 3.2: Test sequences.

PROCESS
• Measure permeability to air on clean, dry core samples and Berea sandstone sample. **Ka**
• **Stabilize temperature of air bath and equipment at 110 ^{0}C for 24 hours.** 1. Saturate samples with 24,000 mg/ℓ brine. o Measure water permeability at 100 % brine saturation. **Kw** 2. Flush samples with crude oil to immobile water saturation, aging overnight. o Measure oil permeability at immobile water saturation. **Ko@Swi** 3. Flood samples with 24,000 mg/ℓ brine to residual oil saturation. o Measure water permeability at residual oil saturation. **Kw@Sor** 4. Flow chemical solutions: o 2 Pore Volumes (PV). 5. Shut-in chemicals overnight. o Re-measure water permeability at residual oil saturation. **Kw1@Sor** 6. Flush samples with the mineral oil (100 PV) to immobile water saturation. o Measure oil permeability at residual water saturation. **Ko1@Swr** 7. Flush samples with brine (100 PV) to residual oil saturation. o Measure water permeability at residual oil saturation. **Kw2@Sor**

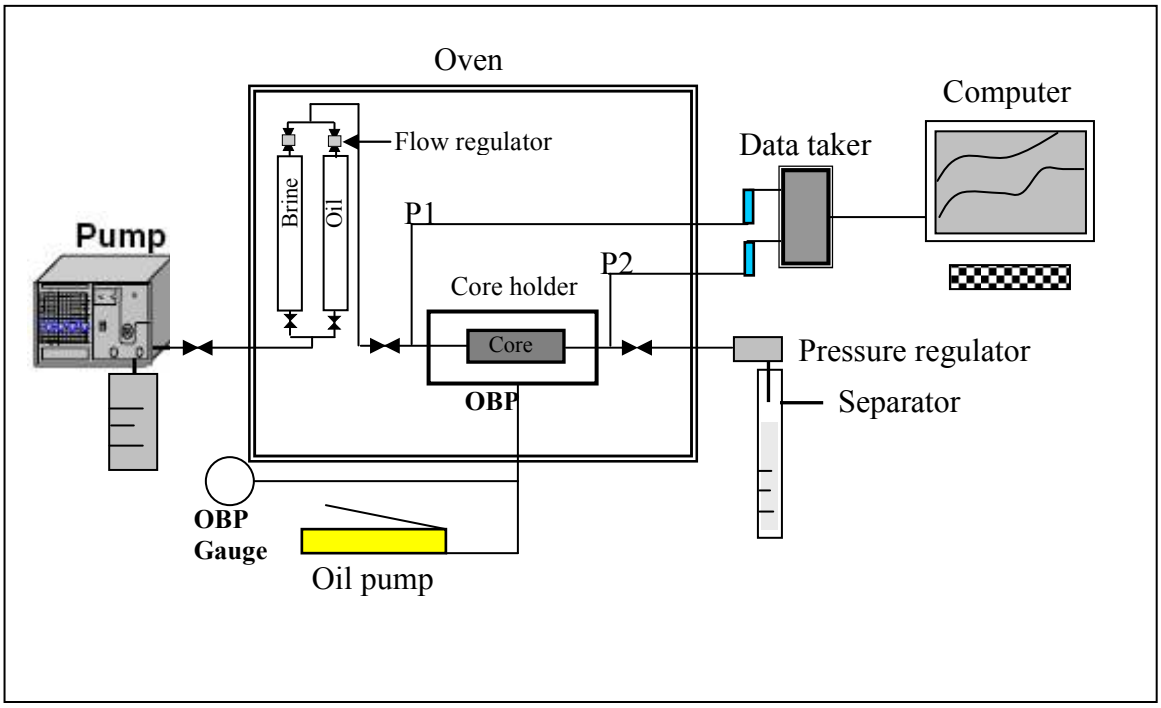


Figure 3.2: Sketch section of core-flooding equipments.

The oil permeability at immobile water saturation (Ko@Swi) and the water permeability at residual oil saturation (Kw@Sor) were measured before chemical injection. After chemical injection (all samples except the control were injected with one of the four chemicals under test) the following measurements were made:

--Kw1@Sor: This permeability was compared directly to the value of Kw@Sor before chemical injection to determine if any reduction in water permeability had taken place.

--Ko1@Swi: This permeability was compared to the value of Ko@Sor measured before chemical injection to determine if chemical treatment had caused an unwanted reduction in oil permeability.

--Kw2@Sor: This permeability was compared to both Kw@Sor and Kw1@Sor to determine if any water permeability reduction resulting from chemical injection (as demonstrated by Kw1@Sor versus Kw@Sor) could be sustained after subsequent oil and water flush cycles (since substantial oil and water flushing of a chemically injected zone would occur around a treated production well in the reservoir).

3-3 Results and discussion:

3-3-1 Results:

The measured permeability for both oil and brine are plotted against the injected pore volume (See Fig 3.3). After chemical placement (Table 3.2 step 4) a course of 100 PV of brine and oil are flushed progressively through the samples to find out the effect; firstly the injection pore volumes and secondly the effect of oil/brine alternation on the chemical strength. Post treatment water permeability (Kw1 and Kw2) trends versus pore volumes are shown in Figure 3.3. And Figures 3.4 and 3.5 showing post permeability reductions in percent (%) for both water and oil cycles. For facilitating the comparison between the results post permeability are calculated in terms of permeability reduction percent (PRP). The permeability reduction for water was considered by comparing water permeability at residual oil saturation (Kw@Sor) to that water permeability resulted after the core samples have been flushed with the subsequent chemicals and oil flushing (Kw1 and Kw2).

$$\text{PRP}\,(\%) = \frac{(\text{Kw@Sor}) - (\text{Kw1 or Kw2@Sor})}{(\text{Kw@Sor})} \times 100 \tag{8}$$

The permeability reduction for oil was calculated by comparing the effective oil permeability at residual water saturation (Ko@Swr) to oil permeability after the samples have been flushed with chemicals (Ko1).

$$\text{PRP}\,(\%) = \frac{(\text{Ko@Swr}) - (\text{Ko1 or Ko2@Swr})}{(\text{Ko@Swr})} \times 100 \tag{9}$$

3-3-2 Discussion:

In brief a point to be noted after flushing the core samples with approximately 15 PV in the course of 100 PV of brine, water permeability at Kw1 and Kw2 for all chemicals was nearly stable, except Reltreat chemical at Kw1 test (See Fig 3.3). Initially RAC and Reltreat chemicals gain strength with time as water permeability (Kw1) decreases with injecting more brine pore volumes through the sample. In contrast, WaterWeb and AquaCon chemicals showed degradation with brine flooding (Kw1) up to 15 PV. This observation reflects that fact some of the chemical broke down during brine flushing through the core samples (See Fig 3.3).

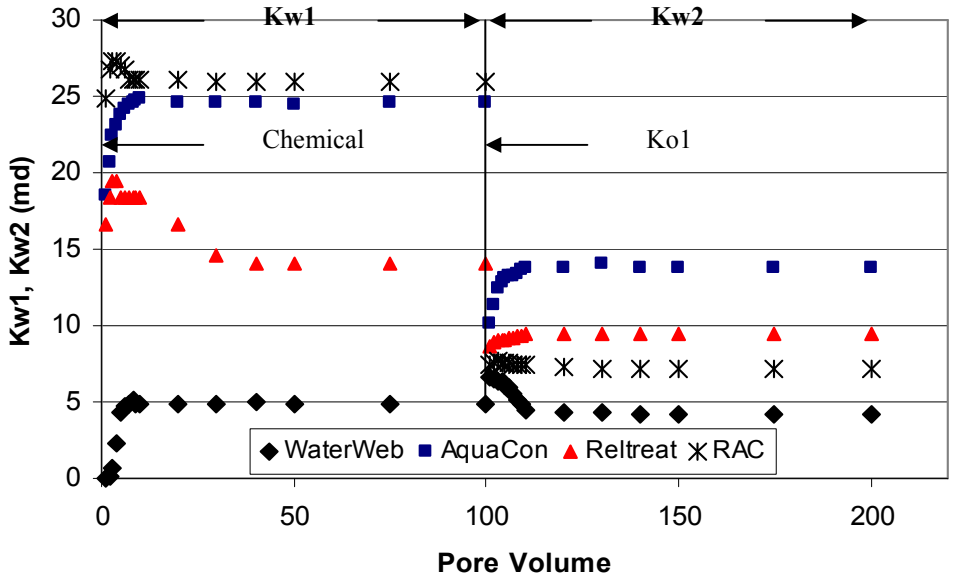


Figure 3.3: Water permeability status after chemicals and subsequent oil, brine flushing.

Detailed discussions of the obtained results from Wanaea core flooding tests are discussed individually based on permeability modification before and after the treatments in term of PRP.

1. **WaterWeb:**

Quantitatively, if comparing the initial permeability of core plug (Kw@Sor) to Kw1 and Kw2 after flooding the sample with WaterWeb chemical, water permeability reduced in a percentage ranging from 61- 67 % for Kw1 and Kw2 respectively, Table 3.3. The reduction in the water permeability is interesting but unfortunately this chemical reduced oil permeability nearly by 60 % in comparison with its initial permeability at Ko@Swr (See Figures 3.4 & 3.5). Therefore this outcome lessens the ability of this chemical to reduce selectively water permeability without marginal reduction in oil permeability.

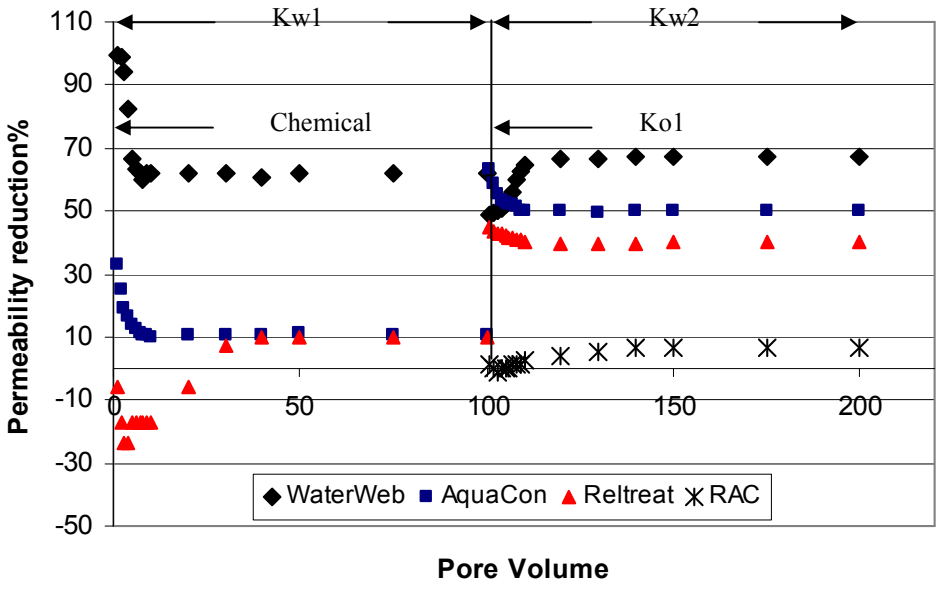


Figure 3.4: Water permeability Reduction for the tested chemicals.

2. **AquaCon:**

While AquaCon chemical has shown more or less the same behavior as WaterWeb, the only difference can be noted was the percentage by which water permeability has been reduced. With AquaCon water permeability reductions are less than WetarWeb (See Fig 3.4) and the percentages were 11 % and 50 % for both (Kw1) and (Kw2)

respectively. Nevertheless, the oil permeability reduction was 48 percent less than WaterWeb, but still it is too high to be of interest.

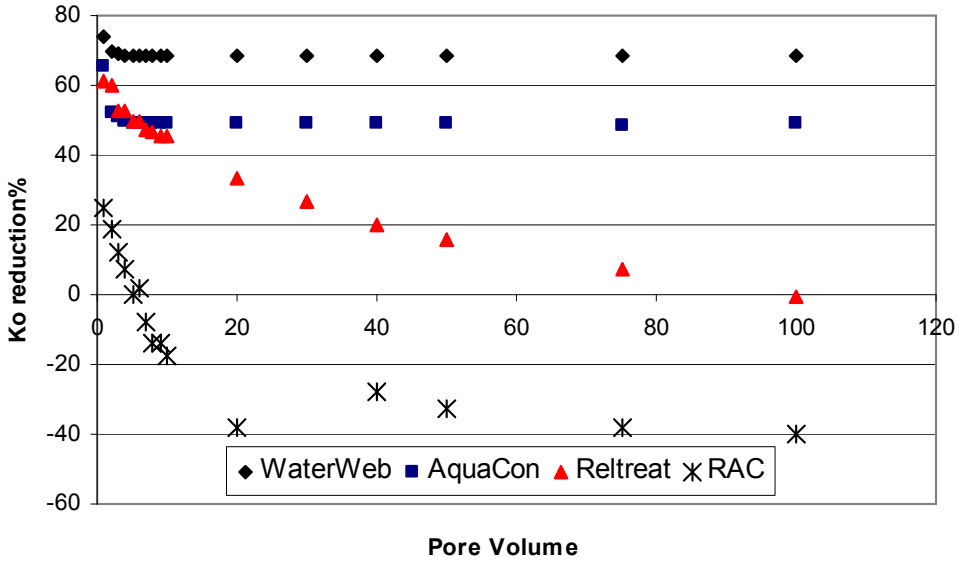


Figure 3.5: Oil permeability reduction for the tested chemicals.

3. **Reltreat:**

In the first 10PV of brine flowing, Reltreat chemical has accelerated water permeability (Kw1), by small increments (similar to Aquacon), see Figure 3.3. While the rest of 100PV of brine flowing showed a slight reduction in water permeability (Kw1). More significantly water permeability reduced (Kw2) after oil and then brine (Kw2) were successively flushed through the sample. The percentage permeability reduced were 10 %, 40 % and -3 % for Kw1, Kw2 and Ko1 respectively. The throughput tests showed that the oil permeability value was initially affected by the chemical injection (Ko1 was only 35.6 md at the beginning of the test), but oil conductivity (Ko1) was regained after flowing significant volumes of oil through the sample.

4. **Curtin Chemical (RAC):**

The tests indicated that this chemical has an effect more like a surfactant in reducing residual oil saturation than a chemical that will reduce water permeability but when oil, then water was subsequently flowed through the sample, water permeability (Kw2) reduced by 6.7 %. In other words, this percentage had a negligible overall Kw-reduction effect. In addition this reduction in water permeability, by this low percentage, probably was because the original (Sor), before chemical treatment has re-established after the second oil flush (Ko1).

During the oil permeability versus oil throughput tests, the value of Ko increased with throughput (as it did with the Reltreat chemical) but the terminal Ko value was much higher than before chemical injection (53.3 md before chemical versus 74.6 md after).

3-3-3 Residual Resistance Factor:

Another method for comparing the obtained results is known as residual resistance factor (F_{rr}). High values of residual resistance factors (F_{rrw}) for brine flow and low F_{rro} values for gas/oil flow means that the chemicals have the ability to control water production with minor effects on gas production. The F_{rr} to brine and gas were determined using equation:

$$F_{rrw} = Kw_{before} / Kw_{after} \quad (9)$$

Where

Kw_{before} =Water permeability before chemical treatments (Kw@Sor).

Kw_{after} =Water permeability after chemical treatments (Kw1 & 2).

The initial threshold for successful treatment is that the F_{rrw} to water should be higher than the F_{rro} to oil (See Fig 3.6). In other words, the ratio to which the oil permeability decreases with chemical treatment should not be as great as the ratio to which water permeability decreases.

However, only Reltreat chemical meets the criterion as it displays low F_{rro} (Ko1) value and high F_{rrw} at the second cycle of brine flushing (Kw2). While according to Seright (2006) for bullhead treatment in the case of no zone isolation, compromising excessive water production by gels in matrix reservoirs that are associated with radial flow will be successful if the gels display residual resistance factor to water greater than 20 and at the same time should display less than 2 for oil (Liang et al 1993; Seright 1988). On the other hand, Zaitoun et al (1989) states that water permeability should not be reduced by a factor greater than 10. Hence the amount to drop water permeability after the treatment is still controversial, so this research work has preferred to select chemicals which can reduce water permeability by a factor ranging betweens 5-15.

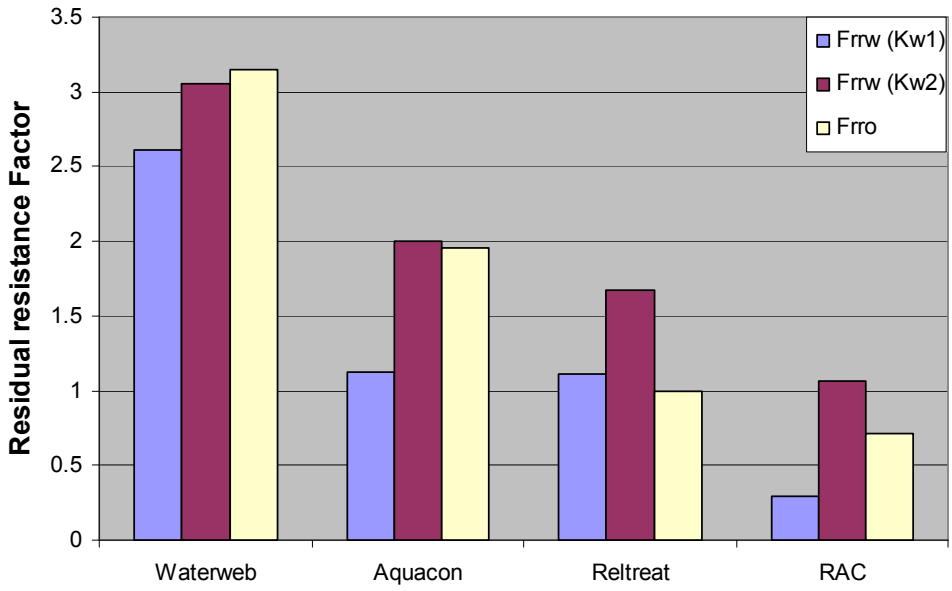


Figure 3.6: Residual resistance factor of brine and oil.

Although the four tested chemicals have shown some permeability modification for treating excessive water in matrix reservoirs they are not an encouraging solution. A point to be noted is that all chemicals have shown higher residual resistance factor when the second water cycle was performed (Kw2) through the core plugs (See table 3.3).

This phenomenon is interpreted as some of the oil re-established in the pore spaces after running Ko1 cycle, therefore has resulted in the lower water permeability during implementing Kw2 cycle. The result of residual resistance factor to water and oil are shown in the Table 3.3, F_{rrw} of the two water cycles Kw1 and Kw2 after the treatment are calculated by dividing the endpoint water mobility of (Kw1 & Kw2) by their initial water permeability at (Kw@Sor). As a result one of these chemicals, Reltreat, is preferred for sequential injection experiments. Even though its residual resistance factor for water is less than the range of this research work limit, the F_{rro} is interesting as it is less than 1.

Table 3.3: Residual resistance factor of two water cycles and an oil cycle.

S.N.	Chemicals	Kw@Sor	$F_{rrw\ 1}$	F_{rro}	$F_{rrw\ 2}$
1	Reltreat	15.7	1.11	0.99	1.67
2	AquaCon	27.6	1.12	1.95	2
3	WaterWeb	12.8	2.61	3.14	3.05
4	RAC	7.6	0.29	0.71	1.08

The summery of the experiment results that have been carried out on the referenced chemicals, WaterWeb, AquaCon, Reltreat, & RAC are given in table 3.4. Chemicals are injected into the core samples after performing step 4. The subsequent steps are post treatment permeability for both water and oil.

Table 3.4: Summery of the test results before and after chemical treatments.

ITEM	MEASUREMENT	PERMEABILITY, md				
		WATERWEB	AQUACON	RELTREAT	RAC	CONTROL
1	Ka	334	291	181	158	260
2	Kw	190	146	127	77.9	195
3	Ko @ Swi	95	82	92.4	53.3	85.6
4	Kw @ Sor	12.8	27.6	15.7	7.6	12.9
5	Kw1 @ Sor	4.9	24.6	14.1	25.9	12.2
6	Ko1 @ Swr	30.2	41.9	93.1	74.6	89.3
7	Kw2 @ Sor	4.2	13.8	9.4	7.1	12.0

Chapter 4

Screening and Rheology

4-1 Introduction:

As one of the main objectives of this research work was to reduce excessive water production in matrix reservoir, the new method of sequential injection could be a promising technique for those wells which have been suffering from matrix flow. The new method, as discussed in the preceded chapters, may control the effect of unexpected post treatment phenomena which are increasing water saturation and cross-flowing. For this purpose, four different commercial chemicals were tested individually under Wanaea reservoir conditions, and resulted low to moderate success in controlling water mobility. As a result only Reltreat chemical is acknowledged for sequential injection test which suggested by this research. Thus, an additional three more different chemicals were prepared with the aim of selecting two more candidate chemicals for applying the new proposed method tests. The additional two more chemicals not only selected according to their ability in reducing water permeability selectively, but also according to their effectiveness under various reservoir conditions. The screening tests are aimed at finding out which factors are chiefly affecting the stability of the chemicals inside porous media. Throughout these tests effects of temperature and brine's salinity, pH, and flow rates are examined against the prepared chemicals.

4-2 Chemicals Preparation:

Three more different chemicals are prepared in WRF laboratory and they are tested for their strength under various reservoir conditions in Berea sandstone. The first two chemicals are primarily composed of commercial water soluble polymers while the third chemical was emulsion and prepared by Professor Amin, Curtin University. The effect of polymer concentrations in the chemicals on permeability reduction has studied.

Table 4.1 shows the detail of chemical compositions and their concentration in water base.

- The concentration of the first chemical (Che-1) in water was 1.2 % and it is prepared by adding 0.7 % Poly (acylic acid), partial sodium salt with poly (ethylene oxide) cross linked + 0.5 % Bentonite into fresh water. For avoiding polymer degradation in the presence of bacteria in fresh water 0.2 % of biocide added to the bulk composition.

- The concentration of the second chemical (Che-2) was 0.8 % in the Nacl brine of 24000 TDS, and it is prepared by adding 0.5 %poly (acrylic acid-co-acrylamide), potassium salt cross-linked + 0.3 % Bentonite into the base solution.

- The emulsion accomplished by agitating one of the phases in to the second phase by means of ultrasonic waves.

The Che-1 and Che-2 are prepared by scaling the amount of Polymer crystal and Bentonite to form 1.2 % and 0.8 % (w/w) of the solution concentration respectively. Then Polymer crystals and Bentonite are slightly added into the flask on the magnetic stirrer that contains the base solution which is either brine or fresh water. The composition was left for almost 48 hours in order to obtain uniform dispersion of the material in the solution.

Table 4.1: The detail of chemical compositions and concentration in the aqueous base.

S.N.	Chemicals	Code	Aqueous Base	Concentration (w/w %)	pH
1	0.7 % Poly (acylic acid), partial sodium salt with poly (ethylene oxide) cross linked + 0.5% Bentonite.	Che-1	Fresh water	1.2	6.89
2	0.5 % Poly (acrylic acid-co-crylamide), potassium salt cross-linked + 0.3 % betonite.	Che-2	Brine	0.8	7.36
3	Emulsion	Em-1	--	--	6.35

The concentration of the polymer for this study, which is for matricial application purposes, has depended on the recommendation made in the previous articles. Some authors (Okasha et al 2001; Wassmuth et al 2004; Zaitoun et al 1989) emphasized that polymers with low molecular weight will be recommended to not exceed its concentration more than 2 % in the bulk solution. Because in applying high polymer concentration for remedy matrix flow, in the case of no zone isolation, the polymer will damage hydrocarbon path severely as much as water path flow.

In this research Bentonite has for the first time been employed in polymer composition. However Bentonite (clay minerals) is known for its high solubility in water as well as its wide range of industrial usage. Utilizing Bentonite in this study was made for the following reasons:

- Increasing the polymer adsorption on the pore grain surface, as confirmed that polymer adsorption increases with increasing clay content in the porous medium,

- Studying the influence of Bentonite in the composition on disproportionate permeability reduction (DPR) behavior, and

- To find out its effect on the chemical strength inside the porous media.

A few papers have been written on applying emulsion for DPR in matrix flow associated with radial flow. One such paper is by Stavland et al (Stavland et al 2006) who have studied two types of emulsifier for bullhead selective water shutoff treatment. They state that it is permissible to inject water based gelant as an emulsion to control fractional water flow. Their idea is that when the designed emulsion is injected into the formation at its static condition will separate in to two phases, an oil phase and water phase. Gelant emerges water phase into its structure that results in water permeability reduction, whereas the oil phase of the emulsion facilitates to the hydrocarbon to flow back through the treated area into the producing well. Whilst employing of emulsion in this research has the same goal but the difference is that this emulsion is not emulsified with gelant. As predicted the viscosity of the water phase, after phase separation, will be greater than brine viscosity, consequently it is considered to hinder brine flow.

4-3 Rheology of the Chemicals:

The rheology study is an important tool for estimating the potential stability of chemicals under different environments. Since reservoir conditions are recognized as being a harsh environment, consideration was given to evaluate the chemicals inside the porous medium for this research work. In most throughput tests for the first water cycle (Kw1) after the chemical injection, water mobility becomes constant with injecting several pore volumes while any subsequent cycles of oil or gas run in between have great impact on the second cycle (Kw2) of water permeability. Hence water mobility (Kw2) is sensitive to the successively flushing the sample with oil or gas after chemical placement.

Therefore, the rheology tests for the prepared chemicals (Che-1, Che-2 and Em-1) are carried out inside the porous medium by assessing their robustness under various conditions of temperature and Brine's salinity, pH and flow rates. Four Berea sandstones were used as the porous medium for the evaluation process. The laboratory analysis determined that their porosity ranged between 14.1-20.4 vol % and their absolute water permeability ranges between 5.5-18.5 md. Each chemical injected into one of the Berea plugs followed the same sequence of throughput tests shown in table 3.2 (with few variations). The fourth Berea sample was used for testing the influence of temperature and Brine's salinity, and flow rates on Che-1. This is because Che-1 displayed high F_{rrw} to water if compared to the F_{rrw} obtained by chemicals (Che-2 and Em-1).

The following are the differences in throughput sequences test for the Berea plugs:-

- All steps from 1-7 in table 3.2 performed consecutively for all chemicals under T = 75 ^{O}C, flow rate = 2 cc/min, brine = Nacl of 24000 TDS, and oil phase= Wanaea oil used.
- After step 7 two phase flow performed in B-1 and B-2. The produced fluids monitored in the separation tube in each pore volume.
- After two phase flow test the temperatures was increased to 125 ^{O}C for measuring Kw3, and Ko2 in some cases.

Table 4.2 shows the petro-physical properties of Berea sandstone used for the throughput tests. The selected core plugs were cleaned by flushing the sample with toluene until the outlet toluene demonstrated clean fluid. Then all Berea plugs were saturated in the brine to measure absolute permeability at 75 ^{O}C. An overburden pressure of 2000 psi was maintained through out all the test procedures.

Table 4.2: Petro-physical properties of Berea sandstones.

S.N.	Berea Plugs	Chemical	Porosity Vol %	Kw T=75C^0, Nacl 24g/L
1	B-1	Che-1	14.1	5.5
2	B-2	Em-1	14.2	8.4
3	B-3	Che-2	19.6	18.5
4	B-4	Che-1	19.4	17.4

4-3-1 Effect of temperature:

Generally high temperature is deemed as one of these factors that causes polymer degradation in the formation. Most of the polymers employed as RPM are effective under 75 ^{O}C (e.g. cationic groups and polyacrylamide backbone (PAAM) (Sorbie 1991)). Aacrylamide groups are known for extreme hydrolysis under higher temperature and the formed polymers become sensitive to divalent cations. Polymer systems are generally enhanced in performance for high temperature application by cross-linking either with metallic cross-linker or with organic crosslinker (Amanullah 2006; Dovan et al 1997; Prada et al 2000; Sanders et al 1994; Vasquez 2004). Accordingly in this study the effects of temperature on chemicals stability are investigated in term of the variation occurring in water mobility with increasing temperature.

1. **Che-1;-**

Figure 4.1 shows post water permeability patterns of Che-1 at two different temperatures, low temperature 75 ^{O}C and an elevated temperature 125 ^{O}C. Kw2 cycle is measured directly after flushing the B-1 with two cycles of brine and oil (Kw1 and Ko) while Kw3 has run after two phase flow test at 75 ^{O}C. A total of

80PV of Nacl (24000 TDS) brine flowed through B-1 plugs at both temperatures. When the temperature was increased to 125 ^{O}C, water permeability (Kw3) slightly reduced from 1.31 to 0.86 md.

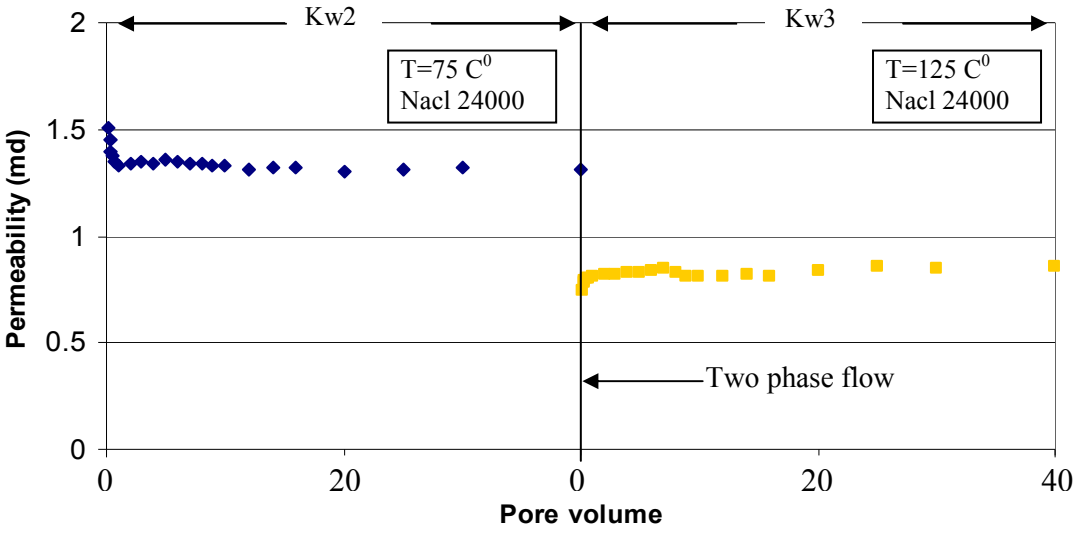


Figure 4.1: Post chemical (Che-1) water permeability trend verses total pore volume injection. Kw2 measured at low temperature 75 ^{O}C and Kw3 measured at an elevated temperature 125 ^{O}C.

This reduction in water permeability at elevated temperature reflects these facts, either this chemical (Che-1) is insensitive to temperature, no hydrolysis, up to 125 ^{O}C or this reduction was caused by re-establishment of oil in the pores space after the two phase flow test at 75 ^{O}C.

The effect of re-establishing oil in the pores space is remarkably obvious when Kw1 and Kw3 are plotted verses PV. In between Kw1 and Kw2 tests three other cycles of the course of 40 PV are flushed, which are Ko, Kw2 and two phase flow. Figure 4.2 shows that water permeability (Kw1) stabilizes at 1.59 md in the end of 40PV and reduced to 0.86 md when Kw3 tests measured at 125 ^{O}C. If comparing water permeability between Kw1—Kw3 and Kw2—Kw3, water permeability reduced noticeably in the case Kw1-Kw3 more than Kw2-Kw3. Thus flushing B-1 with several cycles of brine and oil after chemical injection, water permeability decreases

regardless of increasing temperature. In other word, Che-1 is insensitive to temperature variation up to 125 ^{O}C.

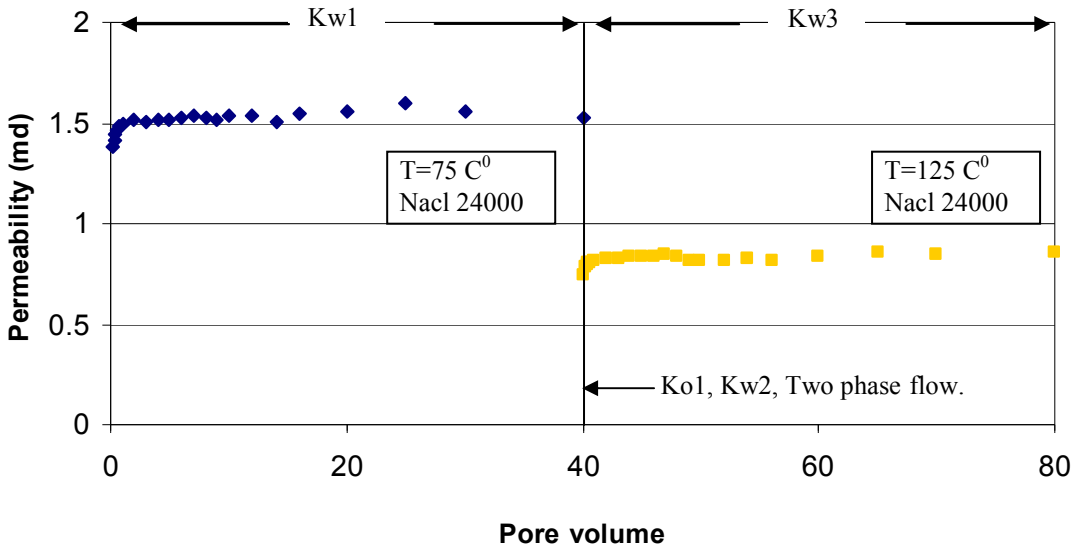


Figure 4.2: Post chemical (Che-1) water permeability trend verses total pore volume. Kw1 measured at low temperature 75 ^{O}C and Kw3 measured at an elevated temperature 125 ^{O}C.

2. Che-2;-

Although the initial water permeability of B-3 is greater than B-1, Che-2 demonstrates the same or less behaviour as Che-1 as it is insensitive to the temperature changes up to 125 ^{O}C. B-3 permeability after chemical injection is well influenced by subsequent flushing of oil and brine like B-1. Each subsequent cycle was composed of 30 PV. Figures 4.3 and 4.4 show post water permeability cycles (Kw1, Kw2 and Kw3) trend of B-3 plotted against the injected PV. Water permeability at increased temperature (Kw3) stabilized at 2.65 md which is less than (Kw2) permeability of 3.32 md. However Kw3 measured directly after Kw2, unlike Kw3 in the case of Che-1 that measured after two phase flow, water permeability (Kw3) at increased temperature is still less than Kw2. In addition Kw3 is significantly less than Kw1 in comparison with Kw2, 2.65 md, 5.78 md and 3.32 md, respectively. It is quite evident that any subsequent flushing will affect the permeability of the medium regardless to changes in temperature. On the other hand

Seright (1994) noticed that the subsequent flushing of CO2 gas affected resorcinol-formaldehyde gel at 41 ^{O}C to loss its strength in the course of 200PV of brine alternating gas cycles. In his study the second cycle of brine permeability has greater value than the first cycle which is measured directly after the resorcinol-formaldehyde gel injection.

In opposite, the chemicals in this research have not shown any sensitivity to water alternating oil cycles to increase water permeability in the second cycles of brine injection. Perhaps this nature of reducing brine permeability in the second cycle of WAO is due to soluble Bentonite in the chemicals. Or these chemical may need more time for gelation and with progressing test time chemicals get strength. It is possible that permeability of the medium effected on gel stability, with increasing the permeability of the rock sample more gel breaks down as the second WAO cycle has performed. For instance Seright run his experiment in Berea sandstones having absolute permeability of 650 md as average. Whereas in this study absolute permeability of the tested Berea sandstone ranged between 5.5-18.5 md. Accordingly absolute permeability of the sample has proportional influence on RPM stability in porous medium.

Moreover it has been found that with decreasing permeability of the medium the chance of DPR will be high as DPR depends on the fraction of gel that controls the flow inside the porous media. Therefore the results from Che-1 and Che-2 tests particularly at second WAO cycle strongly suggesting that most fractions flow of the Berea sandstone (B-1 and B-3) occupied. Because Berea plugs were used in this research have very low permeability in comparison with Bereas employed by Seright.

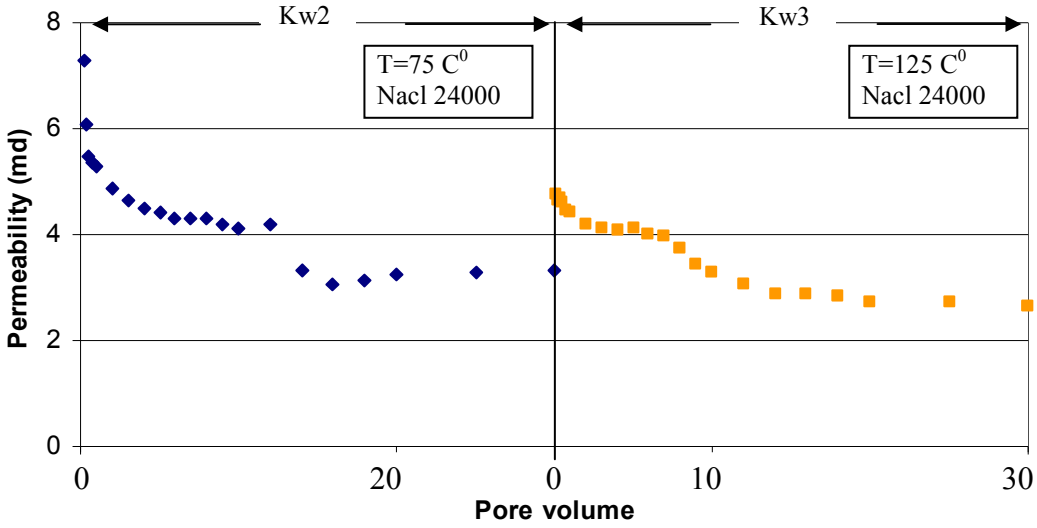


Figure 4.3: Post chemical (Che-2) water permeability trend verses total pore volumes. Kw2 measured at low temperature 75 ^{O}**C** and Kw3 measured at an elevated temperature 125 ^{O}**C**.

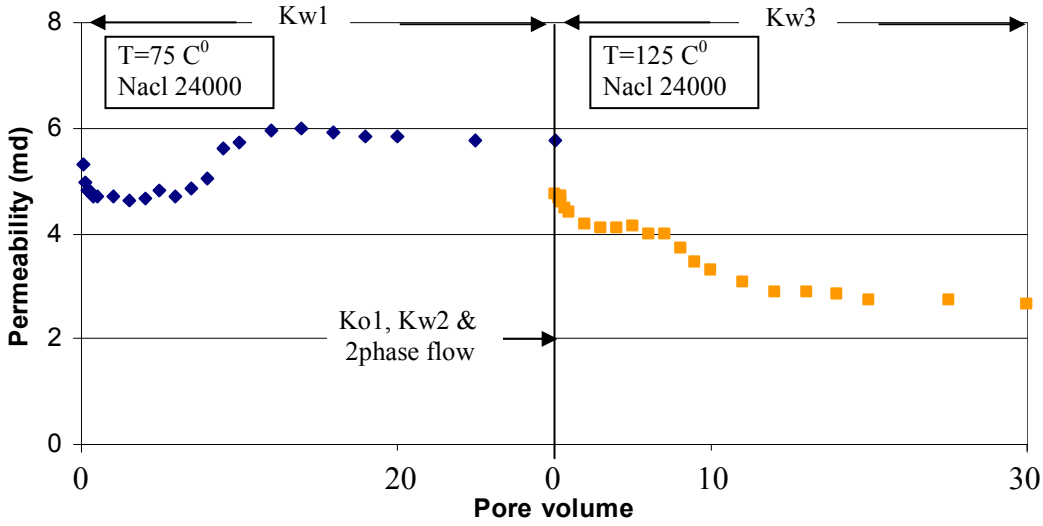


Figure 4.4: Post chemical (Che-2) water permeability trend verses total pore volumes. Kw1 measured at low temperature 75 ^{O}**C** and Kw3 measured at an elevated temperature 125 ^{O}**C**.

3. Em-1;-

The third chemicals (Em-1) shows different attitude with increasing temperature when compared to the first two chemicals (Che-1 & Che-2). Em-1 not only deteriorates with increasing temperature but also with the subsequent flushing cycles

of brine alternating oil. This has been noticed by many researchers as subsequent flushing progress in the porous media, the placed gelant faces shrinkage or decline with flushing WAO/G cycles. Figures 4.5 shows B-2 post permeability trends of two cycles of Kw2 and Kw3 under two different temperatures. The endpoint water permeability of Kw2 and Kw3 are approximately the same, however a cycle of two phase flow had been flushed in between these two water cycles. Although several cycles flushed between Kw3 and Kw1 (e.g. two phase flow and Ko cycles), the end permeability of Kw3 remains higher than Kw1 (See Fig 4.6), unlike the previous tests when Kw3 always displayed lower permeability than Kw1 as a result of WAO cycles. Furthermore end point permeability at Kw2 (4.08 md) is more than at Kw1 (3.07 md) however both cycles performed under the same temperature and only a cycle (Ko) of 30 PV of oil has been run before Kw2 cycle.

This increase in permeability reveals that Em-1 undergoes deterioration with flushing subsequent cycles of brine and oil through B-2, while WAO cycles are measured under the same temperature of 75 ^{O}C.

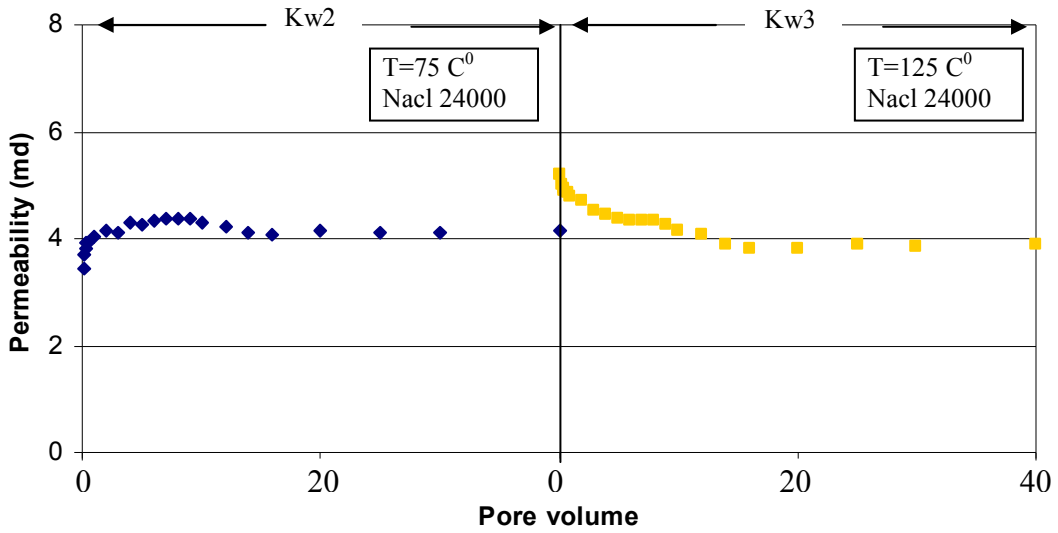


Figure 4.5: Post chemical (Em-1) water permeability trend verses total pore volumes. Kw1 measured at low temperature 75 ^{O}C and Kw3 measured at an elevated temperature 125 ^{O}C.

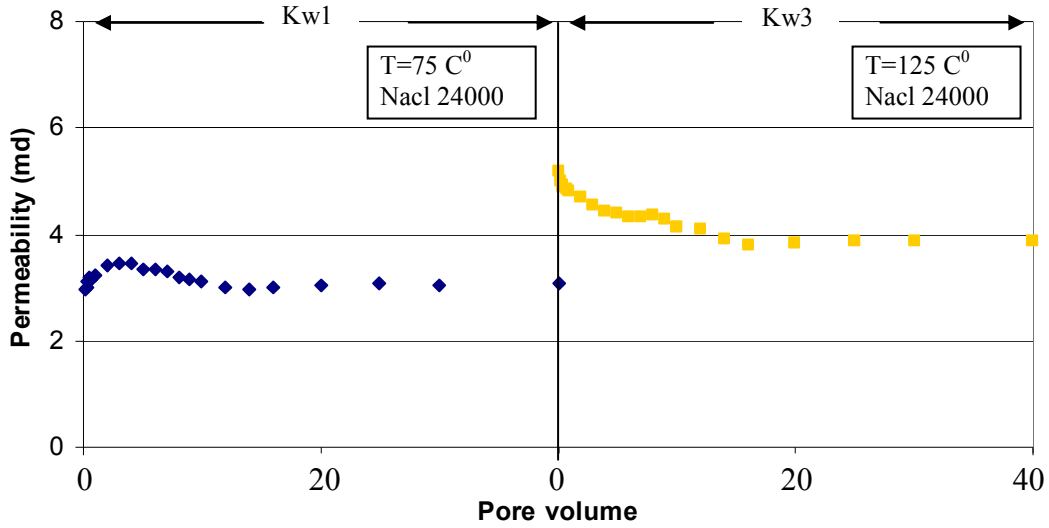


Figure 4.6: Post chemical (Em-1) water permeability trend verses total pore volumes. Kw1 measured at low temperature 75 ^{O}C and Kw3 measured at an elevated temperature 125 ^{O}C.

The effect of temperature on the employed chemicals is shown in table 4.3 in terms of permeability reduction. The permeability ratio is calculated by dividing the endpoint permeability of the subsequent cycles (Kw2 and Kw3) to the first post chemical brine cycles Kw1 and Kw2. The effect of temperature on the chemicals strength is significant and more likely where Em-1 is in situ. The permeability ratios at K3/Kw1 and Kw2/Kw1 for Em-1 are greater than 1. This is meant that with increasing temperature and employing subsequent flushing cycles (WAO), Em-1 is perhaps subjected to hydrolysis inside the pore media. Nevertheless the other two chemicals Che-1 and Che-2 have permeability ratios of less than 1, which is a good indication that these two chemicals are not being affected by temperature variation. On the other hand the slight variation in permeability ratio of the first two chemicals at Kw3/Kw1 and Kw3/Kw2 expose this fact that both B-1 and B-3 are affected by WAO cycles and possibly subjected to change in relative wettablility of B-1 and B-3.

Table 4.3: Permeability ratio of post treatment (Kw) cycles (Brine Nacl 24g/L).

S.N.	Chemical	Kw1(md)	Kw2 (md)	Kw3(md)	Water permeability ratio		
		T= 75C^0	T= 75C^0	125C^0	3/1	3/2	2/1
1	Che-1	1.59	1.31	0.86	0.54	0.65	0.82
2	Em-1	3.07	4.08	3.91	1.27	0.95	1.32
3	Che-2	5.78	3.32	2.65	0.45	0.79	0.57

4-3-2 Effect of Salinity:

The effect of brine salinity and composition was investigated on the Che-1 stability in Berea sandstone (B-4). As Che-1 selectively shows reducing water permeability more than Che-2 and Em-1, further studies were conducted to examine its strength under various conditions such as salinity, pH and flow rate. Several researchers, such as Amro et al (2002), have studied the effects of brine concentration and composition on the chemicals they have used in their study. These authors studied polymer adsorption on rock reservoir at high salinity. They investigated two types of Polymer (PAA and Xanthan) and found with increasing brine concentration both chemicals reduce their viscosity at all shear rate (Amro et al 2002). Mustafa and Turksoy (2001) studied the effects of brine composition and concentration on oil recovery in Garzan crude oil field. They noticed that the recoveries increased with decrease in salinity of the injected brine, but there were little differences in breakthrough recoveries. For instance, when the injected brine was NaCl, oil recovery was increased with the increasing brine salinity up to 30000 ppm, but above this concentration oil recovery decreased dramatically.The effects of divalent cations in brine composition on polymer adsorption on rock surfaces were described briefly in Chapter Two section (2-3-4).

In this research work the objectives behind injecting different brine composition and concentration as throughput after placing chemical were to examine:

- The effect of brine concentration on post treatment permeability of Che-1 in B-4.
- The effect of divalent ion in the brine composition on the Che-1 stability versus the injected pore volumes.
- The effect of multi brine composition on the Che-1 strength through PV injection.

For this purpose four different brines were prepared for injection after chemical placement in B-4. The detail of brine composition and concentration are shown in table 4.4. The same throughput sequence is applied on B-4 at two different temperatures, while the difference is that two phase flow was not performed between K2 and Kw3 (at increased temperature of 125 ^{O}C).

Table 4.4: Brine composition and concentration.

S.N.	Brine Code	Composition	Percent of Components	Concentration (PPM)
1	Sa-1	NaCl	100 %	24000
2	Sa-2	NaCl+KCl	80 % + 20 %	12000
3	Sa-3	NaCl+KCl	80 % + 20 %	24000
4	Sa-4	NaCl+KCl+$CaCl_2$	80 % + 17 % + 3 %	320000

Figure 4.7 shows the permeability trends of Kw1 throughout 100 PV of different brine injection (Sa-1 to 4) at 75 ^{O}C. The test engaged by injecting the different brines consecutively one after another (Sa-1 to 4), after chemical placement in B-4. Sa-1 flushed for approximately 40 PV while other brines just flowed for almost 20 PV.

During flushing Sa-1 permeability normalized at 6.44 md but when it is followed by Sa-2 which has less concentration than Sa-1 and has different composition, the permeability trend in the first 5PV subjected to fluctuation and stabilized at the end of 20PV at 6.8 md.

Furthermore when the concentration increased as Sa-3 flushed post water permeability (Kw1) demonstrated similar behaviour in the first 5 PV as the flowing brine switched from Sa-1 to Sa-2. With progressing time the permeability of Sa-3 gradually stabilized at 7.73 md. In spite of composition when the brine concentration increased to 32000 ppm, Sa-4, brine permeability has not much improved as it is anticipated to be more than the incremental resulted by Sa-2 and Sa-3 if comparing to Sa-1 permeability (See Fig 4.7). The permeability of Sa-4 after flushing 20 PV normalized at 7.96 md. Nonetheless with decreasing brine (Sa-2) concentration to 12000 ppm, the permeability of B-4 increased. Thus adding 20 % of KCl salt to the bulk composition of brine Sa-2 caused Che-1 to experience deterioration, consequently permeability of B-4 increases. In addition brine permeability of Sa-2 and Sa-3 are proportionally increased with increasing brine concentration however they contain 20 % of KCl in their bulk composition (See Fig 4.7).

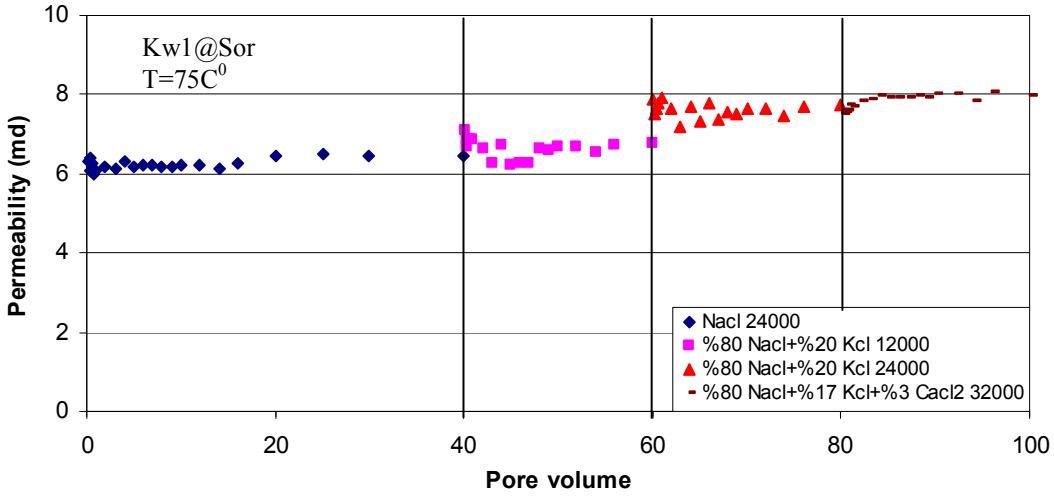


Figure 4.7: Effects of brine composition and concentration on the chemical (Che-1) stability at temperature 75 ^{O}C.

The multi salt brine Sa-4 that include divalent ion Ca^{2+} with a concentration of 32000 ppm did not deteriorate Che-1 in comparison to Sa-2 and 3 brines, however they have less concentration but more chemicals deteriorated during their flowing. Perhaps brine with high concentration 32000 ppm can not pass through the porous media as the brine has low concentration. This similar phenomenon has been observed in the Mustafa and Turksoy (2001) study of increasing oil recovery with decreasing brine salinity.

In order to comprehend the effect of salinity and temperature thoroughly on Che-1 deterioration the same sequence of throughput tests were repeated at higher temperature of 125 ^{O}C. The difference in throughput sequence is that in this test after measuring Kw1 and Ko at 75 ^{O}C the temperature was directly raised up to 125 ^{O}C for measuring Kw3 cycle. Kw2 cycle was not performed at 75 ^{O}C.

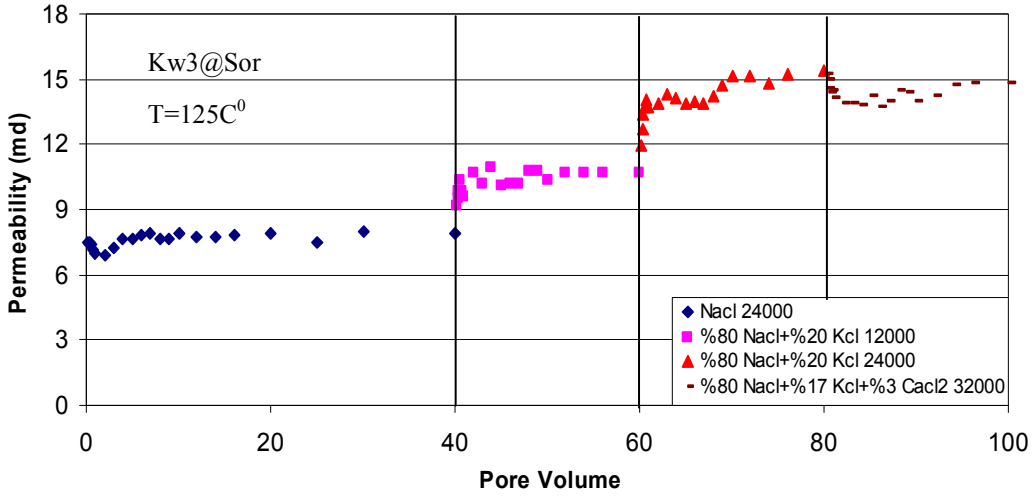


Figure 4.8: Effects of brine composition and concentration on the chemical (Che-1) stability at temperature 125 ^{O}C.

At higher temperature water permeability becomes nearly constant after only 5PV in the course of 40PV of NaCl (Sa-1) flushing and the endpoint water permeability stabilized at 7.95 md (See Fig 4.8). As mono brine switched to Sa-2, Sa-3 and Sa-4

consecutively the trend of brines' permeability increased similar to the test that performed at 75 ^{O}C. But the incremental occurred in water permeability under this temperature 125 ^{O}C is too high if compared to the test performed at 75 ^{O}C. Thus, Che-1 underwent hydrolysis more severely at high temperature incorporated with brine salinity and concentration effects. The endpoint water permeability (Sa-4) rested at 14.87 md after flushing the sample with approximately 100PV. Despite the brine salinity and composition, the effect of temperature is apparent on Che-1 as it deteriorates highly under high temperature (125 ^{O}C). Accordingly, in regards to brine composition Che-1 at high temperature will not be affected rigorously by flowing only mono salt brine. Thus in the preceding paragraphs the effect of temperature on Che-1 was ambiguous because in the previous tests only mono brine NaCl of 24000 ppm was used. As well as, the Berea plugs were flushed with several cycles of WAO before measuring Kw3 at 125 ^{O}C. These two factors minimized the effect of temperature on Che-1. The summary of whole salinity tests and their endpoint permeability of the injected brines are shown in Table 4.5. Moreover the increase that occurred in the brine permeability as the result of salinity and concentration is revealed as Che-1 weakening (See table 4.6). This Che-1 weakening is calculated by subtracting the endpoint permeability of brine Sa-1 to the subsequent endpoint brines permeability Sa-2, 3 and 4 divided by Sa-1 (Eq 10). The data represented in percentage terms for Che-1 to lose its strength as different brine flushed through the Berea sample (B-4). The differences represent the degree of Che-1 weakening as different brine serially injected for almost 200 PV at two different temperatures. Over the whole tests nearly 87 % of Che-1 strength has been lost.

$$\text{Che1-weakening}(\%) = \frac{(K_{Sa-1}) - (K_{Sa-2\text{or}3,4})}{(K_{Sa-1})} \times 100 \qquad 10$$

Table 4.5: Brine endpoint permeability at two different temperatures.

S.N.	Temperature (^{O}C)	Sa-1 permeability (md)	Sa-2 permeability (md)	Sa-3 permeability (md)	Sa-4 permeability (md)
1	75^{0}	6.43	6.8	7.73	7.96
2	125^{0}	7.95	10.71	15.4	14.87

Table 4.6: Effect of brine salinity and temperature on Che-1 strength in term of increasing brine mobility in percentage.

S.N.	Temperature (^{O}C)	Sa-1 endpoint permeability (md)	Che-1 loss (%) Sa-1&Sa-2	Che-1 loss (%) Sa-1&Sa-3	Che-1 loss (%) Sa-1&Sa-3
1	75^{0}	6.43	5.8	20	22.7
2	125^{0}	7.95	34.7	93.7	87

4-3-3 Effect of Flow rate:

As Che-1 losses its strength once subjected to various brines injections, perceiving the effect of flow rate on Che-1 stability is significant to find out Che-1 to what extend can withstand exposure to different flow rates. As this test was performed directly after the salinity tests at 125 ^{O}C, three more PV of Che-1 were injected into B-4 because water mobility regained its conductivity through B-4 to approximately 87 %. Temperature reduced to 75 ^{O}C and Sa-1 is employed to be flowing through B-4 at different flow rates. In the beginning the test water velocity was set at 2 cc/min and the endpoint water mobility stabilized at 5.54 md, while in the previous tests under the same conditions water mobility had higher value of about 6.43 md.

The difference probably was due to the error that came from the pressure transducer readings or from the clogging of some pore spaces as the second injection of Che-1 progressed.

The trends of water permeability with successively increasing and decreasing flow rates are shown in Figure 4.9. The total pore volumes successively injected throughout this test was 53 PV. For each subsequent trial at 3, 4, 5, 6 cc/min increasing or decreasing flow rates 5 PV of mono salt brine (24000 TDS) injected. While at 2 cc/min in the beginning of the test 10 PV flowed and at the end of the test at decreasing rate with the same flow rate only 8 PV was injected.

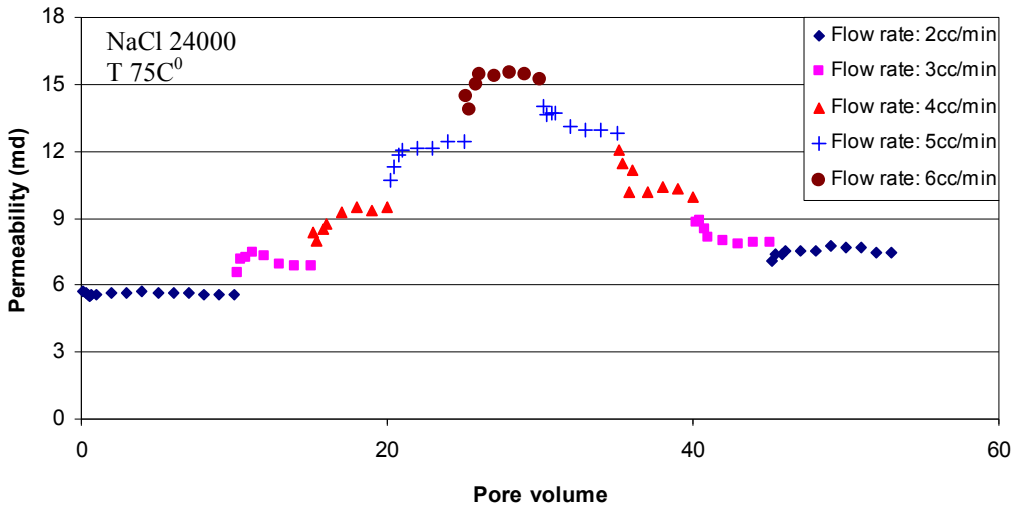


Figure 4.9: Water permeability (Sa-1) trends of successively increasing and decreasing flow rate through B-4.

For explaining the effect of flow rate on the Che-1 strength in porous media, F_{rrw} (residual resistance factor to water) values are plotted against flow rates (See Fig 4.10). These F_{rrw} value are obtained by dividing Kw@Sor before Che-1 placement by the mobility of Che-1 after placement (Kw1@Sor).

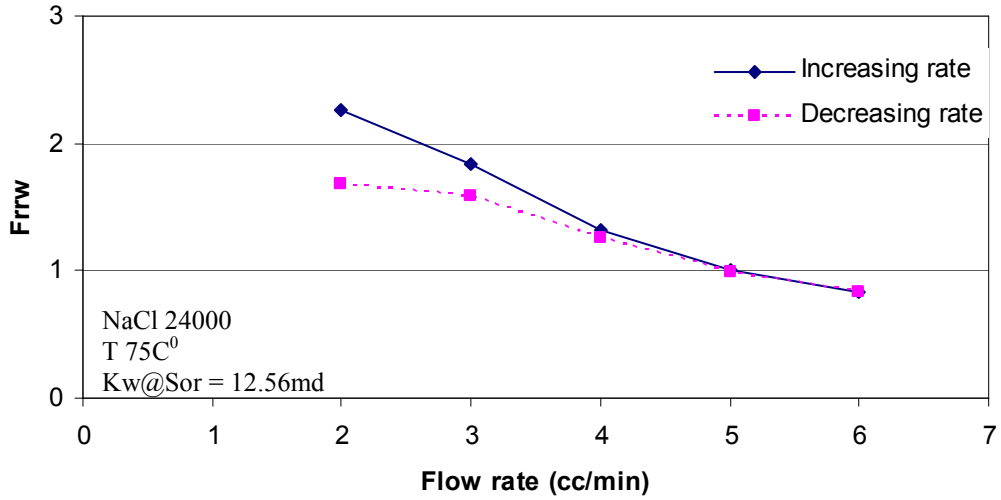


Figure 4.10: Effects of brine injection velocity on Che-1 at 75 ^{0}C**.**

In the first brine injection F_{rrw} was 2.27 at 2 cc/min then the value decreased each time as the flow rate was raised to subsequent higher values (See table 4.7). When the injection rate decreased successively to 2 cc/min, F_{rrw} was 1.69 which is slightly lower than that of at the increased rate. Consequently, this reduction in F_{rrw} suggests that Che-1 experienced breakdown upon exposure to higher flow rates. For expressing the breakdown of Che-1 in percent, equation 10 has been used. The calculation made on the differences occurred in Kw between increased and decreased flow rates at 2 cc/min. The percentage that Che-1 weakened its strength was 25.6 %.

Table 4.7: F_{rrw} of increasing and decreasing flow rates.

S.N.	Flow rate / F_{rrw}	2 cc/min	3 cc/min	4 cc/min	5 cc/min	6 cc/min
1	Increasing rate	2.27	1.83	1.32	1.01	0.82
2	Decreasing rate	1.69	1.59	1.26	0.98	0.82

4-3-4 Effect of pH:

Seright and Matin (1993) had studied the effects of gelation pH on the performance of resorcinol/formaldehyde gel in both core sample and in beakers. They noticed that strong gel formed at pH = 9 while weak gel formed as the pH decreased to 7. In this research work the effect of pH on Che-1 stability was investigated by changing brine pH at inlet before injection into the core sample where the chemical was being placed. In the first step pH of Che-1 was monitored before and after injection to apprehend the effect of B-1 minerals on Che-1 pH. The pH at inlet before injection was 7.68 and at outlet were 7.48. Upon these pH values Che-1 has neutral characteristic and has not been much affected by progressing through B-1 as the pH slightly decrease. In the second step upon the first cycle of brine injection after the chemical placement brine pH at the inlet was 8.86 and at the outlet, pH constantly monitored for almost 40PV, the value approximately ranged from 7.79 - 7.91 (See Fig 4.11). Then after as brine (Sa-1) pH increased to approximately 13.2, brine mobility increased. Correspondingly, as brine (Sa-1) pH decreased to 4.1 water permeability decreased and approximately had the similar brine mobility as the first cycle of brine injection but slightly higher (See Fig 4.11). Nevertheless Che-1 experienced to some extend shear thinning behaviour when the brine's pH changed, but this pH variation resulted to slightly increasing in water mobility, therefore Che-1 has not been greatly influenced by brine pH modification from 4.1 to 12.2.

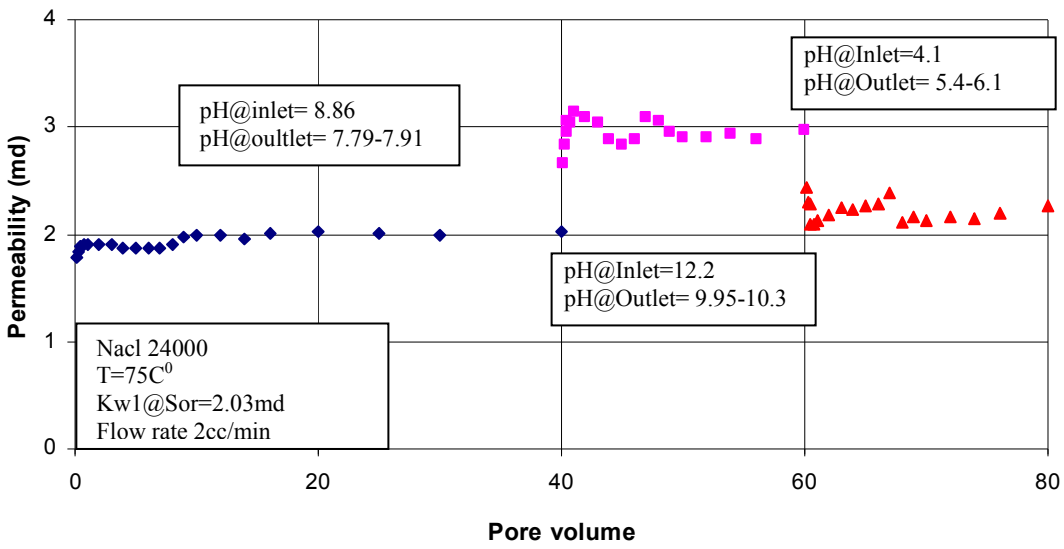


Figure 4.11: Effect of brine's pH on Che-1 stability in Berea core (B-1).

Chapter 5

Candidate Chemicals

5-1 Introduction:

In the prior Chapter the efficiency of Che-1, Che-2 and Em-1 have been investigated under different reservoir conditions. This Chapter aims to present laboratory throughput test results for chemical abatement water and include; firstly, the possibility of applying these chemicals as the candidate for conformance control at residual oil saturation, secondly, the effect and stability of chemicals when two phases are flowing simultaneously, and thirdly, whether injecting single chemical or the proposed new method of injecting several chemicals sequentially is more efficient solution to cure reservoirs that suffering from matrix flow.

Although almost all polymers or gel systems that have been studied in the last two decades are recommended to be utilized for water abatement provided:

- Water and hydrocarbon flows are from different zones,
- Both zones are separated by impermeable layers, and
- In multi layer zones where one of the zones still produce high amounts of hydrocarbon.

But the treatment would be more complicated to apply gel or chemicals in matricial rock when the problem is associated with water displacing oil. The intrusion of the water zone to the hydrocarbon zone will hinder the flow of hydrocarbon and subsequently residual oil saturation increases in the pay zone, such as water Coning or Cusping. To recover the oil paths and reducing water flow steadily, the new method of injecting chemicals sequentially could control water mobility selectively in matrix reservoir. As mentioned this method includes injecting three differing chemicals consecutively into the reservoir rock and over displacing near the wellbore

by the same hydrocarbon fluid that is produced by reservoir. Chemicals are selected for sequential injection test upon their residual resistance factor values; chemicals that demonstrate high F_{rrw} and low F_{rro} are selected. As a result only Che-1 is selected for the test method that suggested by this research.

5-2 Residual Resistance Factor:

5-2-1 Residual Resistance Factor to Water:

- First WAO Cycle:

In the first cycle of water alternating oil, Kw1, at a temperature of 75 ^{O}C with flow rate 2 cc/min and Sa-1 of 24000 TDS, Che-1 demonstrates a reduction in water mobility more than other two chemicals (See Fig 5.1). The values of the first water cycle after chemical placement, F_{rrw1}, for Che-1, Che-2 and Em-1 are 1.25, 0.68, and 0.88 respectively.

- Second WAO Cycle:

The second cycle of water alternating oil, Kw2, performed after Ko1 cycle at temperature 75 ^{O}C with flow rate 2 cc/min and Sa-1 of 24000 TDS. The F_{rrw2} values of both Che-1 and Che-2 increased while Em-1 decreased if compared to their F_{rrw1} values (See Fig 5.1). The values of the second water cycle after chemical placement, F_{rrw2} of Che-1, Che-2 and Em-1 are 1.46, 0.51, and 1.53, respectively.

- Third WAO Cycle:

The third cycle, Kw3, performed at an increased temperature of 125 ^{O}C while the flow rate and brine composition were the same as prior cycles. However as temperature increased Che-1 and Che-1 show high F_{rrw3} to water if compared even to the second cycle F_{rrw2} values (See Fig 5.1). The values of the third water cycle after chemical placement, F_{rrw3}, of Che-1, Che-2 and Em-1 are 2.25, 1.9, and 0.54, respectively.

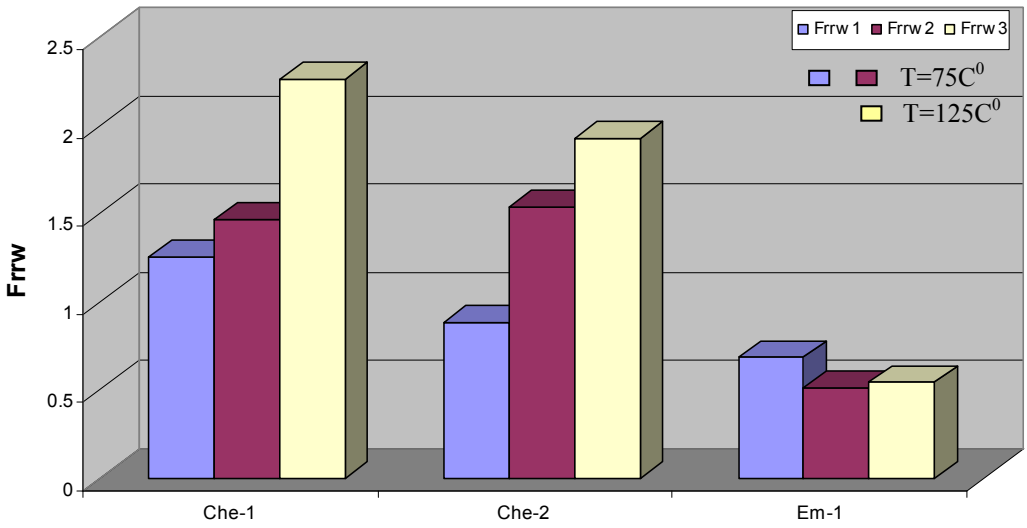


Figure 5.1: Residual Resistance Factor to water of Che-1, Che-2 and Che-3 of three WAO cycles.

Normally, as observed by many researchers, chemicals breakdown as the result of performing WAO cycles after chemical placement and consequently water mobility increases. But in the case B-1 and B-3 where Che-1 and Che-2 were in place, with performing WAO cycles water permeability decreased instead of increasing, the cause of this phenomenon has not been discussed broadly. This outcome could be as the result of:

1. Re-establishing oil in the pore spaces after the treatment and causing water mobility reduction.

2. B-1 and B-3 behave as relatively mixed wettable rock, when the chemicals displace Kw@Sor, the chemical may have affinity to disperse over water wet pores more than oil wet pore.

3. Chemical reactions with oil inside the pores media might plug most of the pores, and

4. Chemicals probably need more time for gelation as in this work only 24 hours (express as hours) has given for chemicals to build up in the rock pores.

To approach and analyse some of the causes that resulted in the decrease in water mobility as WAO cycles have progressed, residual water/oil saturations in the Berea sandstones have been calculated in each cycle from the experiment results. Residual oil/water saturations are calculated at each cycle of water/oil flushing by:-

Measuring *Swr* at 1st cycle at Ko@Swr,

$$Swr = Sw - Pw \qquad 11$$

Where

Sw= Water saturation at Kw (cc), presumed water to fill all the pores after measuring Kw.

Pw=Displaced water volume after measuring Ko@Swr (cc)

Then *Sor* at 2nd cycles at Kw@Sor,

$$Sor = Pw - Po \qquad 12$$

Where

Pw= Displaced water volume after measuring Ko@Swr (cc)

Po=Displaced oil volume after measuring Kw@Sor (cc)

During the chemicals placement a little oil was displaced but it was hard to measure its volume as it has been miscible with the chemicals. Furthmore, as Kw1 cycles performed some small amounts of oil were displaced and Sor corrected to

$$Sor1 = Sor - Po \quad (13)$$

Where

Sor= residual oil saturation at Kw@Sor (cc)

Po=Displaced oil volume after measuring Kw1@Sor (cc)

Thus for *Swr* at Ko1@Swr the equation 11 is used and for the last cycle Kw2@Sor for calculating *Sor* equation 12 is used.

For facilitating the interpretation of the obtained data from the above equations, the data is presented in percentage terms, as shown in Table 5.1. The amount of residual water saturation that retained by B-1 and B-2, after they had been displaced by the first oil cycle, was about two third part of the total volume of their pores. In contrast, B-3 retained water approximately in one third of the total volume of its pores. Regarding Sor all samples demonstrated retention of one third or less volume of oil after displacing by Kw@Sor. While the Sor amount that retained by the core samples are decreased by injecting chemicals as well as by Kw1cycle (See table 5.1).

An important point to be noted is that the post treatment water saturation increased in all core samples after chemical placement. This is a problem predominantly corresponding to water shutoff treatment. Several authors (Elphick & Seright 1997; Liang, et al 1993; Seright & Sydansk 2003) revealed post treatment phenomena to be a serious problem facing water abatement method by chemicals and always it has limited the RPM success in the field. The incremental change that occurred in Swr as the result of chemical injection is variable and depends on the petro-physical properties of the rock formation. For instance, since B-3 has higher absolute permeability (Kw) than B-2 and B-1 it retained less residual water saturation at Ko@Swr. Thereafter water saturation in B-3 increased by approximately 10 % if

comparing Swr values at Ko cycle and Ko1 cycle, i.e. 39.5 % and 49.8 %, respectively. While B-2 and B-1 display higher residual water saturation after the treatment water saturation increased by approximately 3 % for both B-2 and B-1 if comparing Swr at Ko@Swr to Swr at Ko1@Sor values.

Table 5.1: Residual water and oil saturation for the tested Berea samples.

Berea samples	RPM	Swr % Ko@Swr	Sor % Kw@Sor	Sor % Kw1@Sor	Swr % Ko1@Swr	Sor % Kw2@Sor
B-1	Che-1	69.4	25.0	22.2	72.2	24.1
B-2	Em-1	71.4	21.4	19.5	74.5	23.6
B-3	Che-2	39.5	31.5	29.8	49.8	23.5

With reference to the results given in Table 5.1, the first possible explanation is re-establishing oil in the rock pores, to reduce water mobility after chemical placement has lessened as oil saturation Sor at Kw2 decreased or slightly increased. The second cause is most encouraging as the B-1and B-3 retained high water saturation in their pores as well as Swr increased after chemical placement. The third proposed cause could not be interpreted by increasing and decreasing water/oil saturation. The fourth reason is considerable, which could be the chemical requiring more time for gelation, as there were not any remarkable change in wettability during implementing WAO cycles.

5-2-2 Residual Resistance Factor to Oil:

Candidate chemicals should demonstrate residual resistance factor to oil of less than 2 when the aim is to control water mobility in matrix reservoir associated with radial flow in the case of no zone isolation (Liang et al 1993; Seright 1988). All chemicals lie in this rang of residual resistance factor which is less than 2 (See Fig 5.2). But

only Che-1 and Che-2 have minimized the water mobility after their placement. Accordingly Che-1 has been considered for further tests as it shows higher residual resistance factor to water than those of Che-2 and Em-1.

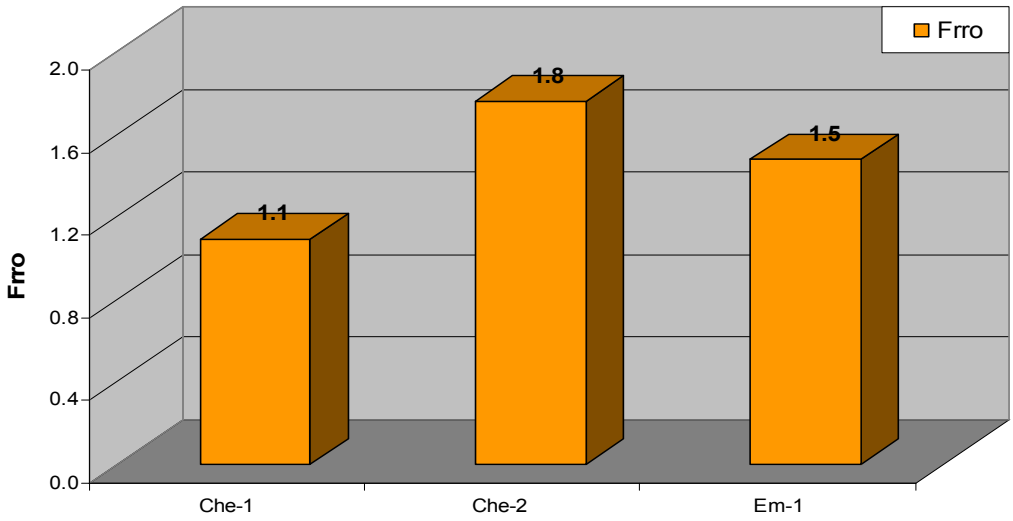


Figure 5.2: Residual Resistance Factor to cured oil for Che-1, Che-2 and Em-1 at 75 ^{0}C.

5-3 Chemicals Injectivity:

Candidate chemicals are selected according to their ability to selectively reduce water permeability but their injectivity for field application remains a problem. Chemicals demonstrating injectivity problems can not be applied in a tight zone or a low permeable zone, because chemicals may only penetrate a few centimetres in the reservoir rocks. The term resistance factor has been used for implying chemical injectivity and can be determined by using the following formula (Kohler & Zaitoun 1991):

$$RF = \frac{\Delta Pc}{\Delta Pw} \qquad 14$$

Where;

ΔPc = pressure difference across the core sample during chemical injection, having the same flow rate of brine, psi.

ΔPw = pressure difference across the core sample during brine flowing at residual oil saturation flow, psi.

The chemicals that have been examined in this study in general have not met injectivity problems (See Fig 5.3). Since resistance factor values are lower than two, chemicals can flow in these medium at least with the same mobility of brine at residual oil saturation conditions. Therefore these chemicals are appropriate for injection in a reservoir having matrix nature grains.

Due to the differences of chemical composition and concentrations Che-1 and Em-1 displayed higher resistance factor than Che-2 (See Fig 5.3). This result is coinciding with Che-1 as the concentration of polymer in its structure is more than Che-2. Hence chemical injectivity is inversely proportional to polymer concentration. Moreover to determine the optimum volume of chemicals to be injected, pressure difference (ΔPc) verses injected chemical pore volume graph, as developed from this research work, has been used.

When ΔPc value is normalized, injecting more pore volumes will not affect the value of ΔPc . It is then considered that the core plugs have totally been saturated with chemicals. The optimum volume for Che-1, Em-1 and Che-2 to be injected in the field is approximately three pore volumes (See Fig 5.4).

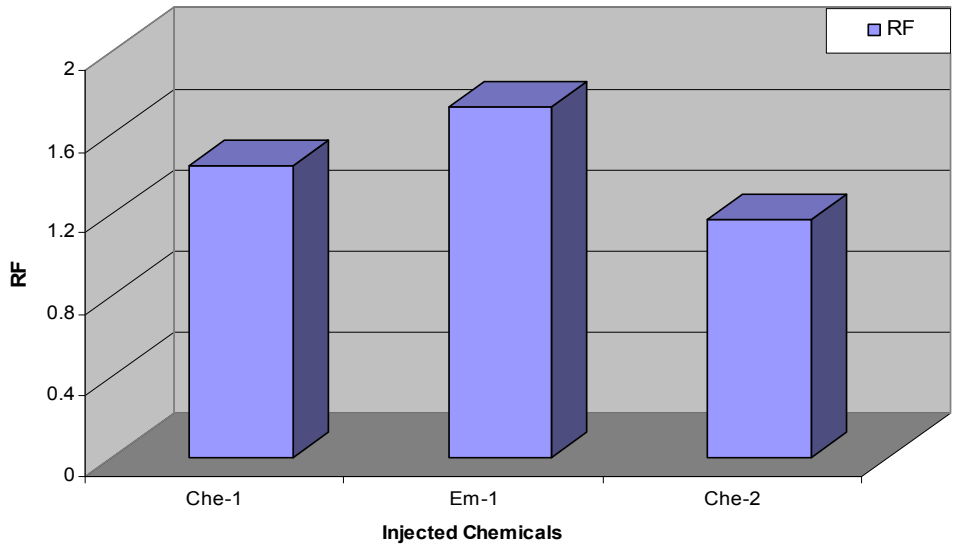


Figure 5.3: Resistance factor of the injected chemicals.

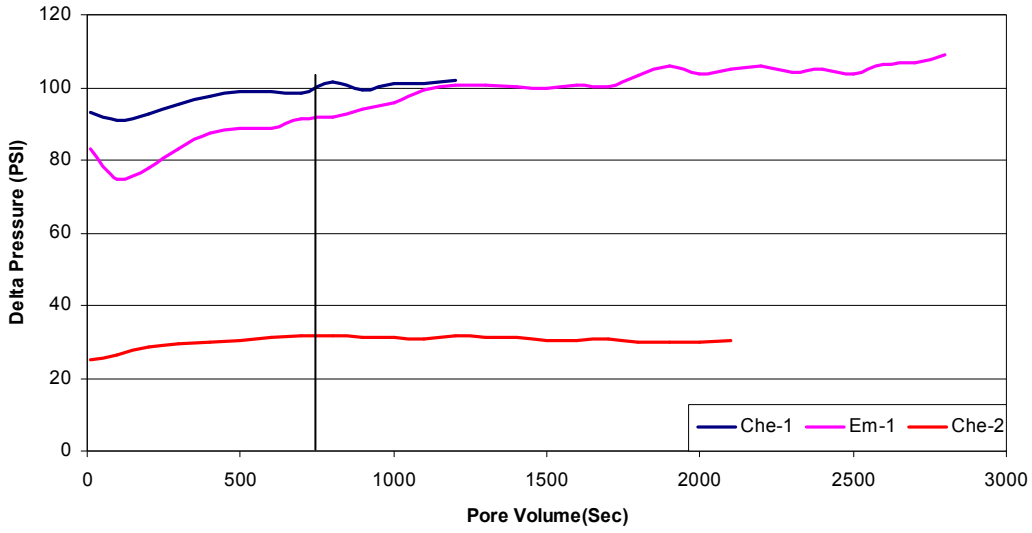


Figure 5.4: Pressure difference verses PV of the injected chemicals.

5-4 Two phase flow tests:

Following the Kw2 cycle, two phase flow tests are performed on each Berea samples, B-1 and B-2 at temperature $75C^0$. The purpose of this test is to examine the resistance of chemicals if two phases' oil and water are simultaneously flowing through the rock pores where chemicals are in situ. The experiment is implemented by flushing the samples with both phases having the same flow rate before injecting into the Berea plugs. To ensure that both phases have the same flow rate before injecting into the Berea plugs, the following steps are considered:

- The flow rate before displacing oil and water in the cylinders was 2 cc/min.
- After they have been displaced in the cylinders, before flushing the Berea plugs, the flow rate should be 1 cc/min per phase.
- To achieve an accurate flow rate of 1 cc/min, a needle valve (meter flow valve) has been installed on both phases.
- The volume of the co-produced fluid for their individual phases is checked several times before inflowing into the Berea samples (See Fig 5.5).

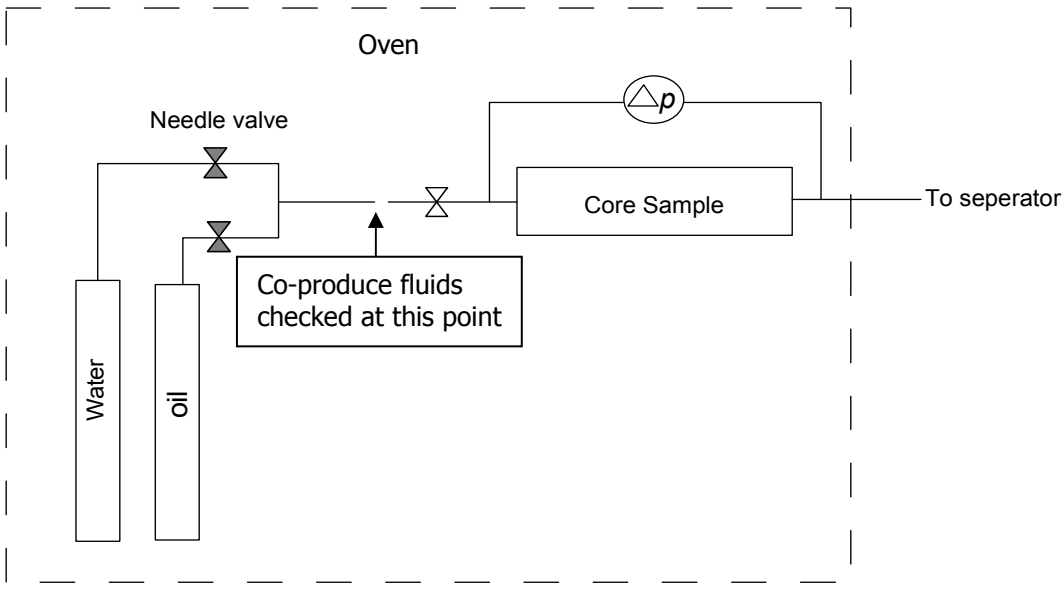


Figure 5.5: Schematic sketch on how two phase flow experiments is performed.

After flushing the Berea samples the volume of the co-produced fluid in the separator is measured for oil and water amounts at each single pore volume. Approximately a total of 15 pore volumes were injected, and the pressure differences across the core sample were monitored.

5-4-1Che-1 in situ:

Figure 5.6 shows the result of two phase flow test where Che-1 is in situ, the two phases have flowed through B-1 with the same flow rate, and each phase had 1 cc/min (total 2 cc/min). After B-1 was flushed with two phases' oil and brine simultaneously, B-1 produced more oil than water in the separator. The percent of oil produced in each pore volume was approximately about 80 % whereas brine composed only 20 %. This result could be an indication that the Che-1 maybe reducing water production during flowing both oil and water simultaneously through B-1. However this test is not implemented before chemical placement, to define the effect of Che-1 on the two phase flow, but still this difference between oil and water percentage is supportive for this conclusion that Che-1 can hinder brine flow more than oil.

On the other hand, B-1 has shown relatively high water wet rock medium, as it retained water in its pores of about 72 % when it has been flushed to residual water saturation at Ko1@Swr cycle (See table 5.1). Thus the rock wettability could be facilitating oil production more than brine production in B-1. Finally this outcome could be the result of contributing the effects of Che-1 and rock wettability.

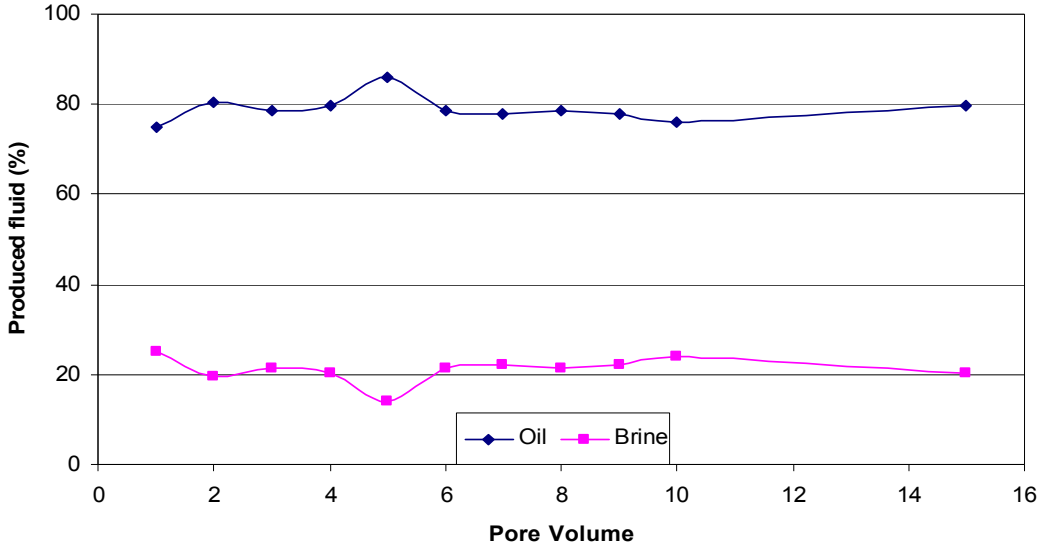


Figure 5.6: Result of two phase flow test in B-1, the volume of the produced fluids (oil and brine) displayed in percent; it is performed after Kw2 cycle at temperature 75 ^{O}C.

5-4-2 Em-1 in situ:

Figure 5.7 shows the result of two phase flow conducted in B-2 where Em-1 is in situ, similarly more oil was produced than brine but the percentage is different. The percentage of oil and brine that was co-produced in a single pore volume was noted to be about 60 % and 40 % respectively. Although this ratio of oil to brine is less than the ratio of oil to brine in the previous test, B-2 demonstrated to be relatively high water wet rock like B-1. The B-2 hold water in its pore of about 74 % as it has been flushed to residual water saturation at Ko1@Swr cycle (See Table 5.1).

This lower ratio of oil to water is an indication that chemical Em-1 revealed less potency to reduce water mobility than Che-1. In addition the pressure difference across B-1 was higher than the pressure difference across B-2 as the fluids oil and brine flooded the plugs with the same flow rate (See Fig 5.8).

It has been known that high pressure difference value is an indication of low mobility rate, thus Che-1 resisted the conductivity of the injected fluids through B-1 pore medium more than Em-1 in B-2.

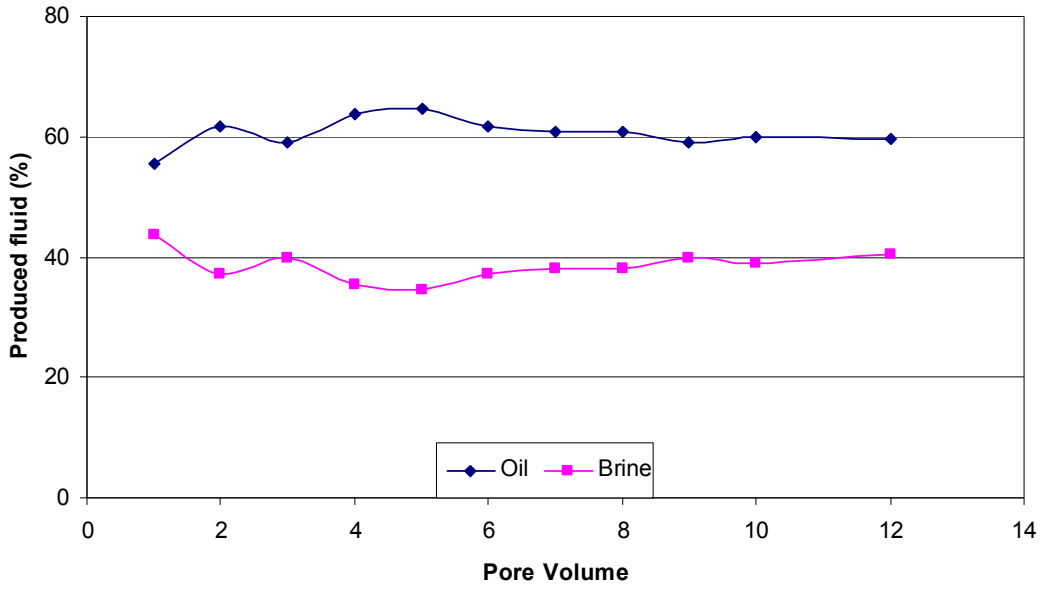


Figure 5.7: Result of two phase flow test in B-2, the volume of the produced fluids (oil and brine) displayed in percent; it is performed after Kw2 cycle at temperature 75 ^{O}C.

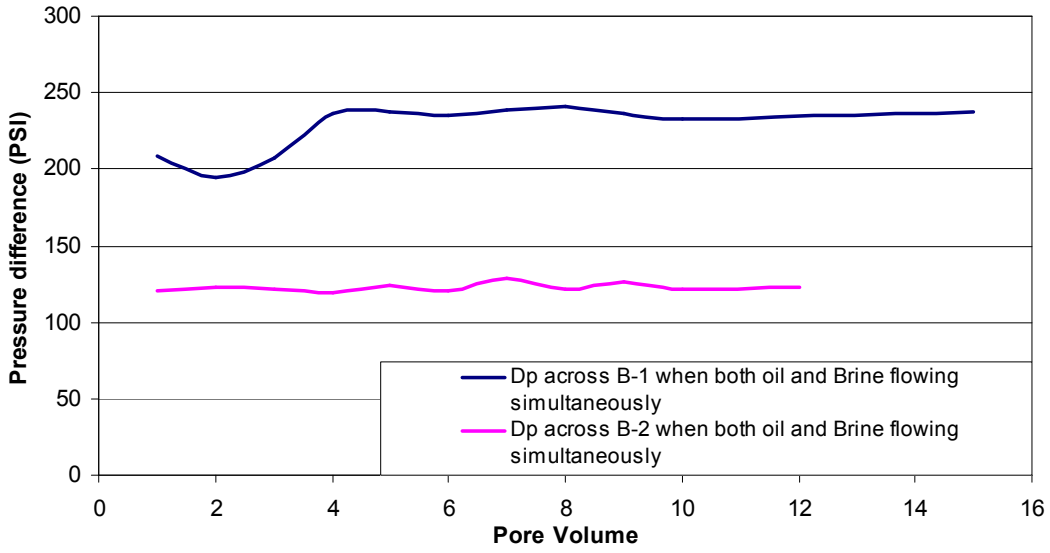


Figure 5.8: Pressure difference across B-1 and B-2, two phase flow tests.

Due to the two phase flow implemented directly after Kw2 cycle, it maybe considered that the Kw2 cycle had affects on the oil and brine flowing in to the pore spaces, because the Berea pores were observed to be saturated mostly with brine. Therefore after the first cycle of two phase flow test, B-2 was flushed with three pore volume of oil to find out if the preceded Berea saturation had any influence on the

final result. Figure 5.9 shows the result of the second cycle of two phase flow after B-2 being flushed with three pore volume of oil. The percentage of producing oil to water dramatically changed where oil increased progressively approximately from 60 % to 80 % while water production reduced from 40 % to about 20 %.

This outcome, which resulted in an increase in oil production, occurred just after flushing the B-2 sample with only three pore volume of oil. Nonetheless, it could hold only one interpretation that oil during propagation in B-2 has formed an oil path through the chemical zone. This phenomenon has been described by Seright (2006) as oil forming a worm path like in the chemical.

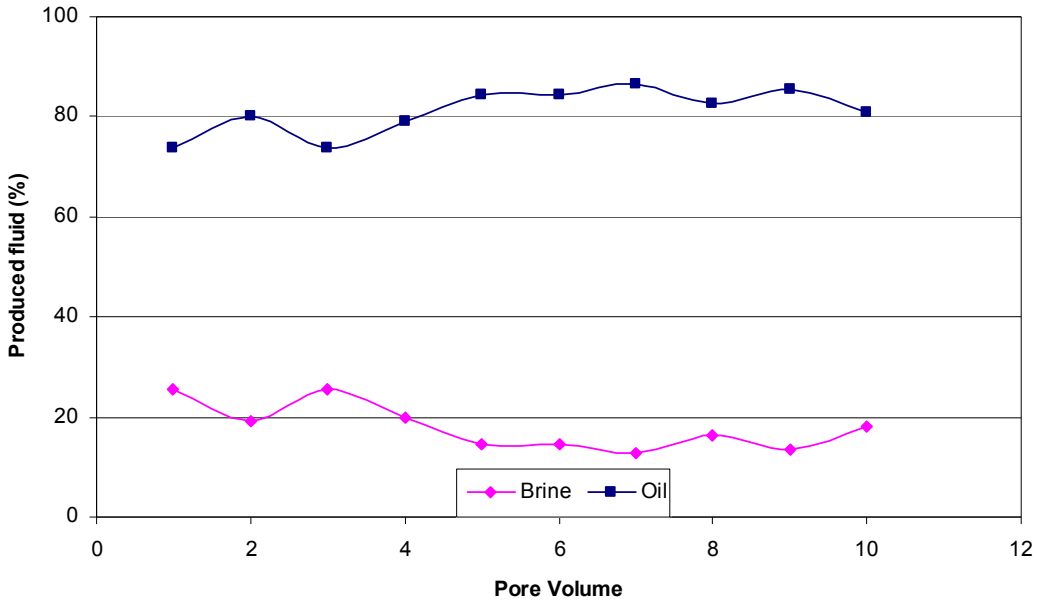


Figure 5.9: Two phase flow test in B-2 at temperature 75 ^{O}C; performed after it has been flushed with three pore volume of oil. Oil production increased as the result of flushing the sample of three pore volume of oil.

The above result is encouraging to the recommendation to over displace chemicals by hydrocarbon after they have been placed in the reservoir rocks. As well as depending on this result for the new method tests, which is injecting chemicals serially, over displacing chemicals by oil should be performed before running Kw1 cycle. This displacement will facilitate oil to inter-finger through the placed chemicals and consequently will lead to enhance oil flow after the treatment.

Chapter 6

New Method Test

6-1 Introduction:

The aim of this research is to reduce excessive water production in oil and gas wells that are suffering from matrix flow. To achieve the aim of this research work the new method of injecting chemicals sequentially is acknowledged. Therefore it is of great importance to theoretically perceive how this method will work to reduce water mobility in porous media. From the literature review two different theories are discussed, fluid partitioning theory and wall effect theory, on how injected polymer functions to reduce water permeability inside porous media. The method proposed through this research work is based on the wall effects theory. This theory concludes that a thin layer or film of gel covers the pore walls and pore throats which then decrease the actual pore size. **Mannella et al (1998) have calculated mathematically the thickness of formed gel on the pore walls using the following equation.

$$t_\rho = f(\Delta)\sqrt{K_{before}} \qquad 15$$

Where;

t_ρ=Polymer layer thickness

$f(\Delta)$ = it is a permeability percent reduction $\{100\times(K_{before}-K_{after})/K_{before}\}$

According to the above equation the thickness of polymer straightforwardly depends on the percent of water permeability reduction. Thus its thickness increases with reducing post treatment water mobility. As known from literature, water mobility reduces extensively with increasing polymer concentration. Furthermore this study considers matrix reservoirs however recognized as a homogeneous medium, but their pore size and pore throat are unlike.

Consequently injecting a single chemical with a certain concentration may plug the tiny pores and reduce the effective size of larger pores (See Fig 6.1).

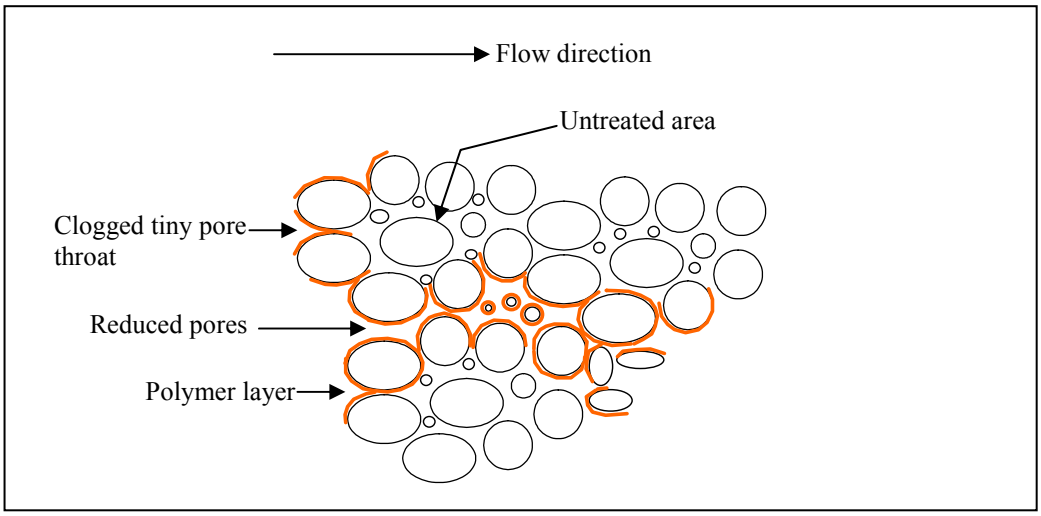


Figure 6.1: Schematic distribution of the polymer layers on the pore walls of the treated pore regions.

On performing Kw2 after the treatment, always some of the polymers will breakdown and gradually water mobility increase with progressive flooding of the core sample over time. Presumably the most polymer breakdown expected to be coming from layers that have plugged the tiny pores. Apparently the injection pressure at the tiny pores, because they are clogged, becomes greater than pressure at the reduced pores. As these layers are considered being fragile films, with constantly increasing injection pressure across the treated area, these layers are destructing continuously until the injection pressure gradually decreases to nearly the resistance of the polymer layers. For imaging this scenario under field conditions when the affected well is suffering from matrix flow and is being treated with a single chemical two phenomena could be happening:

1. An impermeable layer exist between the pay zone and offensive water zone;-

- When the treated wells allow back to production, initially water production has reduced dramatically.
- After the treated wells back to production for a while, the reversed pressure decline across the reservoir starting to plunge down again. Then water mobility will gain its ability to flow through the plugged, tiny, pores. Consequently water finds a path through these tiny pores to the untreated area that are located behind the clogged, tiny, pores (See Fig 6.2).

2. No impermeable layer exist between the pay zone and offensive water zone

- Initially after the treatment if the chemical layers were strong enough to resist the fluid pressure of the intrusive water body, it will look for another path consequently cross-flowing occurs into the oil zone.

In addition it has been found that the disproportionate permeability reduction depends on the amount of polymer dispersed or absorbed by the porous rock. If a single polymer has been employed, it cannot penetrate deep into the formation rock and saturate most of the pore spaces. Because polymer during its injection into the reservoir formation immediately starting to build its layer on the surface of the rock grains. As a result the tiny pores are plugging initially which then creates an obstacle for the polymer to flow. Consequently the polymer flow will turn off to find another path and its dispersion will be uneven. Since the tiny pore are plugged by polymer some large pores that maybe located behind them will left untreated as the polymer turned off from its path. Accordingly the displacement of polymer over the rock porous will no be piston like. Once fluid flows back through the rock reservoir its production increase with destroying more polymer layers at tiny pores that behind them untreated large porous. Finally it facilitates water to compete its production with hydrocarbon again after the chemical treatment (See Fig 6.2).

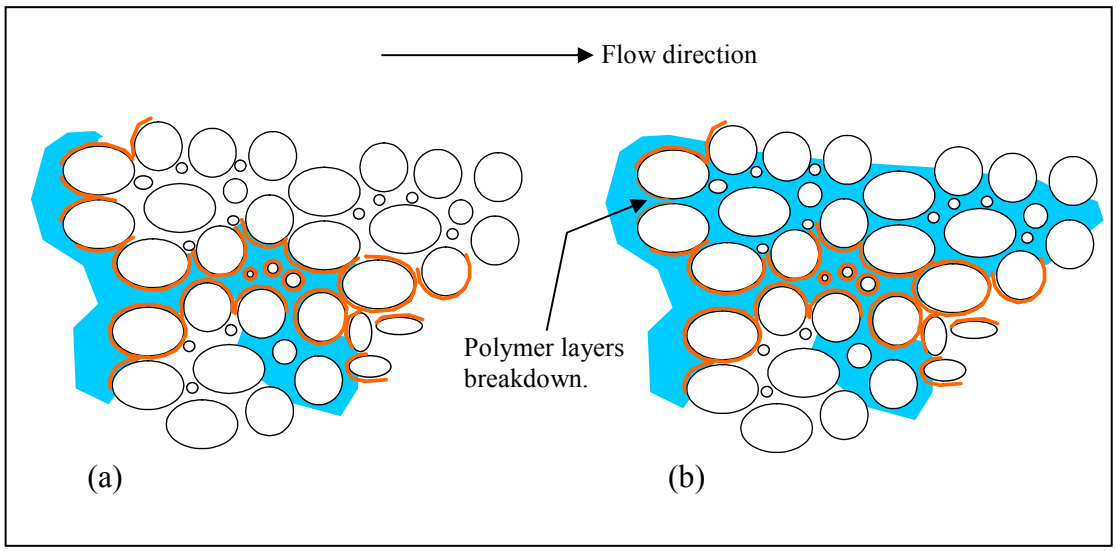


Figure 6.2: Schematic scenarios of post treatment results; (a) brine flow directly after the treatment, (b) brine flow as the polymer breakdown at tiny pores.

The placements of several chemicals around the affected well have the following advantages:

- Chemicals can penetrate deep into the formation as the first chemical has low polymer concentration,
- The dispersion of chemicals in the pores will be more homogeneous if compared to single chemical injection,
- As three different chemicals were used presumably most of the pore space will be treated during the chemical injection,
- Minimizing the possibility of occurring post treatment impact, such as cross-flowing,
- It can be applied in matrix reservoir with out zone isolation whether or not an impermeable layer exists between the pay zone and offending zone, and
- It is expected to reduce water permeability gradually and steadily over a longer time than for single chemical treatment.

6-2 Test Method:

The test condition has followed the same test procedure conditions as was performed with the B-1, B-2 and B-3. The temperature was 75 ^{O}C and an over burden of 2000 psi maintained on the Berea sample during the whole of the test sequence. The sequence of injection is similar to the previous tests except that instead of injecting one chemical three chemicals are injected sequentially in to the Berea sample. Then Kw2 and Kw3 cycles are flushed. Temperature at Kw3 increased to 125 ^{O}C as the earlier tests. The petrological properties of the Berea plug used for this test can be found in Table 6.1.

6-2-1 Candidate chemicals:

The chemicals used for this test have been chosen according to the prior test results. Depending on the results Che-1 demonstrated to be more likely to reduce water mobility selectively more than the other chemicals. Consequently Che-1 is preferred for the first injection with approximately the same concentration as Che-1 when it was tested in B-1. For the second chemical, the same Che-1 formula was chosen but the polymer and Bentonite concentration are increased in the solution to compose 1.5w/w of the bulk chemical solution. The last chemical, Reltreat was selected due to its ability to reduce water permeability without affecting oil permeability, as displayed in the tests that had been implemented for the Wanaea reservoir.

Table 6.2 shows the composition and concentration of the candidate chemicals. The first two chemicals (SCh-1 and SCh-2) are prepared in the WRF laboratory following the same preparation procedure for Che-1 and Che-2 for the earlier testes. The Reltreat chemical is prepared by its provider elsewhere.

Table 6.1: Petrophysical properties of Berea plug that used for injecting chemical sequentially test.

S.N.	Berea Plugs	Chemical	Porosity Vol %	Kw $T=75^0C$, Nacl 24g/L
1	B-5	SCh-1+SCh-2+Reltreat	20.4	34

Table 6.2: Details of chemicals composition and concentration that used for injecting chemicals sequential tests.

S.N.	Chemicals	Code	Base	Concentration (w/w %)	pH
1	Poly (acylic acid), partial sodium salt with poly (ethylene oxide) cross linked + Bentonite.	SCh-1	Fresh water	1.1	7.81
2	Poly (acylic acid), partial sodium salt with poly (ethylene oxide) cross linked + Bentonite.	SCh-2	Fresh water	1.5	7.72
3	Reltreat	Reltreat	----	----	7.60

The volume of each chemical (SCh-1, SCh-2 and Reltreat) that had been injected successively into B-5 are shown in table 6.3. Initially one pore volume of SCh-1 was injected into B-5 directly, followed by 0.66 PVof Reltreat and 0.5 PV of SCh-2. The over displacement process between the chemicals are expected to be immiscible because they have different concentrations, as given in Table 6.2. Thus SCh-1, SCh-2 and Reltreat were placed in B-5 and 24 hours given for gelation.

Table 6.3: Volume of the injected chemicals into B-5.

S.N.	Berea Plugs	Berea Pore Volume (CC)	Injection Volume (PV)		
			SCh-1	Reltreat	SCh-2
1	B-5	13.6	1	2/3	1/2

6-3 Results:

6-3-1 Chemical dispersion:

Figure 6.3 shows pressure difference across B-5 when the three chemicals were consecutively injected into the sample. The first chemical (SCh-1) did not meet any difficulties during propagation into the pore spaces as it demonstrated low pressure differences across B-5 and stabilized at 21psi. When SCh-1 over displaced by Reltreat the delta pressure initially increased to reach 120 psi. With more Reltreat injection the Dp decreased noticeably and stabilized at 25 psi. This plunge in Dp as more Reltreat was injected can be interpreted as Reltreat making a pathway, like worm paths in the ground, through the first (SCh-1) skin. It was noted that Reltreat has not dispersed evenly throughout the B-5 pores; it had only found its existing path to the outlet.

On the other hand, SCh-2 seemed to have been distributed more evenly as the Dp increased with continuously injecting more volume of SCh-2 into the B-5. Therefore it was expected the displacement being piston like during its propagation in B-5 where both SCh-1 and Reltreat skins are in place. Consequently the Dp across B-5 increased and its value normalized at 144 psi. Depending upon the Dp results, chemicals are considered more likely to be distributed uniformly throughout B-5 pore spaces. However the worm-path like is expected during Reltreat injection.

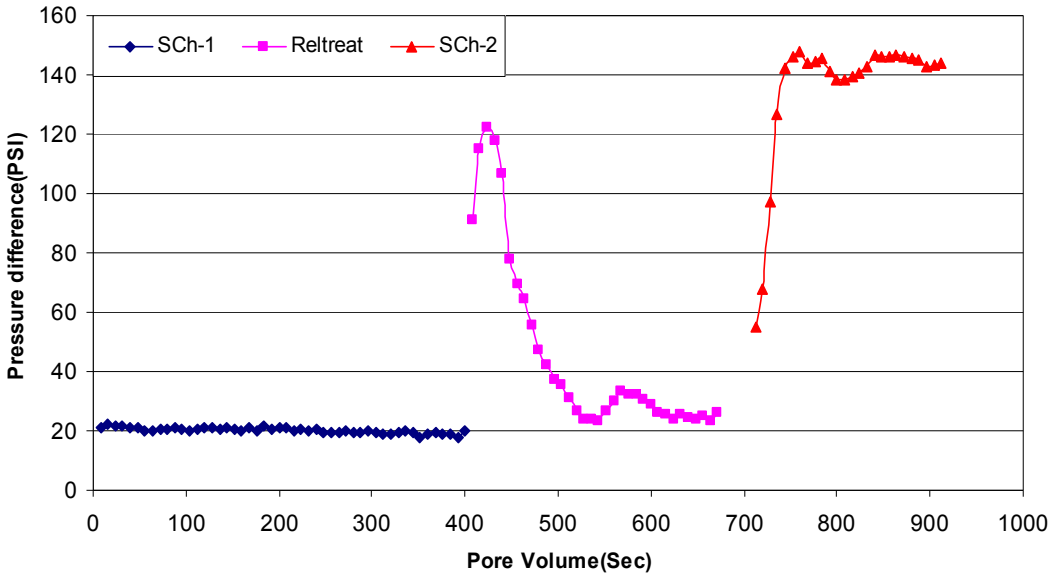


Figure 6.3: Pressure difference across B-5 as the SCh-1, SCh-2 and Reltreat injected progressively at temperature 75 ^{O}C with flow rate of 2 cc/min.

6-3-2 Flow modification:

Following the chemicals injection step (SCh-1, SCh-2 and Reltreat) they over displaced by oil depending on the result obtained from the previous test, which determined over displacing chemicals by oil will enhance oil mobility after the treatment. When the post treatment water cycle engaged (Kw2) in B-5, water permeability conspicuously reduced if compared to post water permeability in the cases when the same chemicals tested individually in both Berea plugs and Wanaea cores. For instance, residual resistance factor to water at B-5 is obviously higher than these at B-1, B-2, B-3 and Wanaea cores (See Fig 6.4). The enhancement that occurred in F_{rrw} as the result of injecting chemicals sequentially into the B-5 is displayed by the dash line in Fig 6.4. The ratio by which F_{rrw} to water increased at three cycles of brine flushing (Kw1, Kw2, and Kw3) for this test is compared to the results obtained by injecting chemicals individually represented by:

F_{rrw}= F_{rrw}@Sequential test / F_{rrw} @Individual test 16

For the first cycle, the F_{rrw} value of sequential injection tests was approximately five times higher than the F_{rrw} for a single chemical injection in the case of Che-1 and Reltreat chemicals. For the second cycle F_{rrw} for this test method was still 2.5 times higher than F_{rrw} obtained for single chemical injection tests. Once the temperature increased to 125 ^{O}C more chemicals breakdown occurred and resulted to low F_{rrw} through the application of the injecting chemicals sequentially test. However, F_{rrw} of Che-1 increased at the test performed at high temperature but still it is less than the F_{rrw} of this test. The F_{rrw} value at Kw3 for this test method is 2.95 while for Che-1 and Che-2 are 2.25 and 1.9, respectively. As a result of these observations it was concluded that to obtain advanced conformance control by chemicals in matrix reservoir injecting chemicals sequentially is recommended provided each subsequent injected chemical has a higher viscosity.

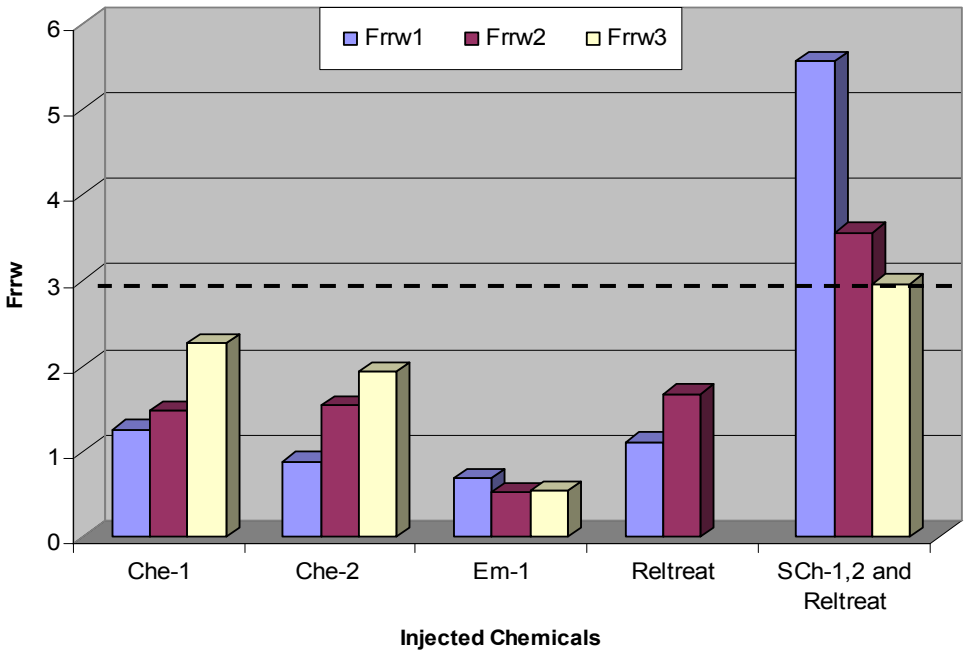


Figure 6.4: Residual resistance factor to water for the tested chemicals. F_{rrw1} & F_{rrw2} performed at temperature 75 ^{O}C while F_{rrw3} performed at 125 ^{O}C.

As a rule of thumb, chemicals are preferred to be the candidate for conformance control if they selectively reducing water mobility without any significant affect on oil conductivity in the rock formation. In addition to this improvement which occurred by applying the new method for reducing water permeability, oil mobility was marginally affected. For example Figure 6.5 shows the residual resistance factor to oil of the tested chemical. The value of F_{rro} of the new method is still beneath the outstrip limit, which is two, for determining candidate chemicals according to the literatures. Therefore applying this method for conformance control in a matericial reservoir can be used to enhance the potential of RPM performance.

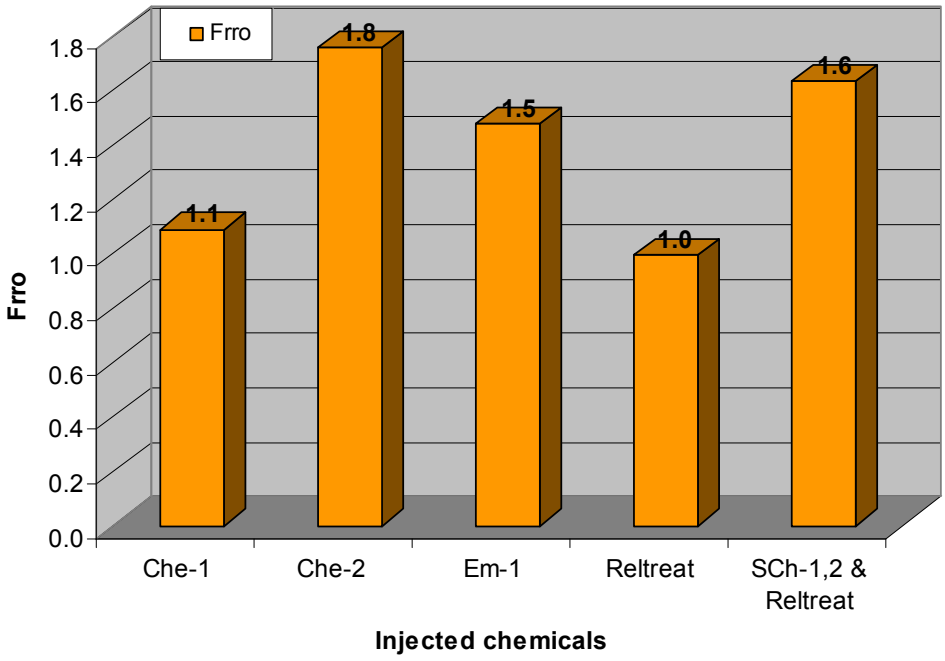


Figure 6.5: Residual resistance factor to oil for the tested chemicals at 75 ^{O}C.

Chapter 7

Conclusion and Recommendation

7-1 Conclusion:

The results from this research work provide an analysis of advance water abatement in hydrocarbon reservoir where the wells suffer from matrix flow. From the experiments conducted the following conclusions have been made:

Chapter 3:

1. For attacking excessive water production in Wanaea oil field chemical abatement is acknowledged as a solution over the mechanical isolation.
2. Throughput tests can provide an indication of a chemicals' validity under reservoir condition, because it simulates the actual reservoir conditions during the test.
3. The four recently developed chemicals tested against the core plugs from Wanaea oil field have demonstrated some permeability modification. The chemicals were prepared by WaterWeb, Reltreat, AquaCon, and Curtin University WRF.
4. However, only the Reltreat chemical meets the criterion as it displays low F_{rro} (Ko1) value and high F_{rrw} (Kw1) value. But according to Seright (2006) candidate chemicals, for healing matrix flow in the case of no isolator layer between the zones, should demonstrate a high F_{rrw} value of at least 20 while F_{rro} should not be greater than 2.
5. Hence these chemicals can not be functional for curing wells that have been experiencing excessive water production from radial flow.
6. Only Reltreat has been selected for the injecting chemical sequentially tests.

Chapter 4:

7. Since reservoir conditions are recognized as being a harsh environment, this research was conducted to evaluate the chemicals inside the porous medium. The Che-1, Che-2 and Em-1 chemicals were prepared and tested for their rheology under various conditions of temperature, salinity, flow rate, and pH inside the rock pores.
8. Both Che-1 and Che-2 are more likely to be insensitive up to 125 ^{O}C as the subsequent brine cycle (Kw2 and Kw3) decreased its mobility.
9. Em-1 was noted to be sensitive to temperature as water mobility increased with increasing temperature.
10. Water alternating oil cycles have crucial influence on B-1, B-2 and B-3 wettability since water mobility decreased as three WAO cycle progressed.
11. On the other hand, the chemicals in this research work have not shown any sensitivity to WAO to increase water permeability in the second cycles of brine injection, as noticed by other researchers. This variation may be due to the nature of reducing brine permeability in the second cycle of WAO to soluble Bentonite in the chemicals.
12. As different brines were flushed serially, Che-1 deteriorated as water mobility of B-4 increased from 6.44 to 7.96 md at 75 ^{O}C, while at a higher temperature (125 ^{O}C) Che-1 deteriorated severely when flushed by different brines. This resulted in an increase in water permeability from 7.95 to 14.87 md.
13. Mono brine (NaCl) has not much effect on the stability of Che-1 as its mobility was noted as being constant after only flushing 5PV. However, it has high concentration of 24000 TDS.
14. Brine Sa-2 that contains 20 % of KCl with 12000 TDS concentration, caused Che-1 to experience notable deterioration, consequently permeability of B-4 increased.
15. With increasing brine concentration (Sa-3) up to 24000 TDS, Che-1 breakdowns increased more than that of brine Sa-2.

16. The multi salt brine Sa-4 that include divalent ion Ca^{2+} , having concentration of 32000 ppm, does not deteriorate Che-1 as much as was made by Sa-2 and Sa-3, however they have less concentration.

17. Upon the brine tests Che-1 lost nearly 87 % of its strength inside the pores medium with flushing of approximately 200PV at two different temperatures of 75 ^{O}C and 125 ^{O}C.

18. Despite of the brine salinity and composition, the effect of temperature is apparent on Che-1. It is deteriorated significantly under high temperature of 125 ^{O}C more than that of the test performed at 75 ^{O}C.

19. Che-1 in B-4 was subjected to flow rate tests. The tests required flushing NaCl brine of 24000 TDS at 75 ^{O}C. After increasing and decreasing flow rates Che-l lost approximately 25.6 % of its strength.

20. The results from pH tests confirmed that Che-1 to be stable under various ranges of pH from 4.1 to 13.2.

Chapter 5:

21. In the first cycle of water alternating oil (WAO), Kw1, at temperature of 75 ^{O}C with flow rate 2 cc/min and Sa-1 of 24000 TDS, Che-1 demonstrates an ability to reduce water mobility more than the other chemicals applied. The values for the first water cycle after chemical placement, F_{rrw1}, of Che-1, Che-2 and Em-1 were 1.25, 0.68, and 0.88 respectively.

22. In the second cycle, F_{rrw2} values for both Che-1 and Che-2 increased while Em-1 decreased when compared to their first cycle F_{rrw1} values. The values of the second water cycle after chemical placement, F_{rrw2} of Che-1, Che-2 and Em-1 were 1.46, 0.51, and 1.53 respectively.

23. Although the third cycles was performed at an increased temperature of 125 ^{O}C, Che-1 and Che- 2 displayed high F_{rrw3} to water, even if compared to the second cycle F_{rrw2} values. This phenomenon probably has a number of explanations such as increasing the affinity of the Bereas to retain more water in its pores than oil.

24. The F_{rrw3} values of the third water cycle after chemical placement, of Che-1, Che-2 and Em-1 are 2.25, 1.9, and 0.54 respectively. These values are obviously higher than the F_{rrw} of the second cycle.

25. To approach and analyse some of the causes that resulted in decreasing water mobility as WAO cycles progressed, residual water/oil saturations in the Berea sandstones were calculated for each cycle from the experimental results.

26. According to the percentage of Swr and Sor resulted in B-1 and B-3, it seems that the cause of re-establishment of oil in rock pores after chemical placement to reduce water mobility has been lessened, as oil saturation Sor at Kw2@Sor decreased or slightly increased in B-2.

27. Both B-1 and B-2 were noted to behave more like water wet rocks, retaining water more than oil in their pore space. This led to a reduction in water mobility. By performing WAO, Swr has increased slightly in both Berea plugs.

28. Chemical gelation may require a greater retention time within the core, as there were not any remarkable changes in wettability during implementing WAO cycles.

29. All chemicals F_{rro} value lies in this range of selecting candidate which is less than 2, but only Che-1 and Che-2 have minimized the mobility of water after chemical placement.

30. Accordingly Che-1 was considered for further testing as it showed higher residual resistance factor to water than Che-2 and Em-1.

31. The results from two phase flow test are encouraging for the process of over displacing chemicals with hydrocarbon after chemical placement in reservoir rock.

Chapter 6:

32. The Dp values across the B-5 plugs during chemicals injection reveal that the chemical distribution in B-5 pores are more likely to be uniform, however a worm like path was expected during Reltreat injection.

33. The post treatment water permeability (Kw1) in B-5 is conspicuously reduced when compared to the cases of a single chemical only being injected in Berea plugs and Waneaea cores.

34. The residual resistance factor to water at B-5 is obviously higher than for the B-1, B-2, B-3 and Wanaea cores.

35. This enhancement occurs by injecting these chemicals sequentially into the B-5. As a result for obtaining advanced conformance control by chemicals in matrix reservoir, injecting chemicals sequentially is recommended provided through injection their viscosity should be increasing correspondingly.

36. As a rule of thumb, chemicals are preferred to be the candidate for conformance control if they selectively reduce water mobility without any significant effect on oil conductivity in the rock formation. Oil mobility was noted to be marginally affected with this method.

37. The value of F_{rro} of the new method is still beneath the outstrip limit of two for determining candidate chemicals according to the literature.

7-2 Recommendation:

- Introducing bentonite in the chemical composition is required for both reducing actual pore size and increasing the absorption of polymer by the formation rocks.
- The screening of chemicals inside the pore space for field application is recommended because reservoir conditions are considered as a harsh environment.
- Over-displacing chemical by oil after placement is crucial since the laboratory results confirmed oil mobility was enhanced by over-displacing chemical by oil.
- For enhancing the performance of the injected chemicals, such as RPM, a new technique is indeed required. The injecting chemicals using sequentially method for field application is recommended over injecting a single chemical for curing matrix flow.
- To optimise the performance of the new test method, further extensive study are required to be implemented on different chemicals having different concentrations of polymers.
- In this study only three chemical were sequentially injected. This resulted in an enhancement for the control of water mobility. Employing five or six chemicals possibly may give a better outcome.
- The tests were performed in a Berea plug with length of 7.16cm and diameter of 3.42cm. It is recommended that further tests to be performed using larger core plugs for determining the optimum volumes of the chemicals that are required for injection.
- Scanning of the core plug after chemicals placement is recommended to find out how the chemicals are distributed through the core pores.
- For obtaining homogeneous distribution of the chemicals inside the porous medium, nearly piston like displacement is needed once chemicals are injected sequentially.

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Appendix

Test results

Permeability calculations

$$K = u.\mu.L \,/\, \Delta p.A$$

Where:

K= Permeability to liquid, darcies

L= Sample length, cm

u = Flow rate, cm^3 per second

Δp = Pressure difference across the core sample, atmospheres

μ =Viscosity, centipoise

A=Cross sectional area, cm

Appendix tables:-

The gathered data from this research work are shown in 10 tables; from table a-1 to a-2 data of through put tests of Wanaea core flooding are shown. While from table a-3 to a-10 data of single chemical injection and injecting chemical sequentially are presented. Moreover, tables from 5 to 7 shows post treatment water permeability at various Brine salinity and composition, flow rates and pH injection.

Table a1: Post treatment *Kw&Ko* versus injected PV for the tested chemicals in Wanaea cores (T=110 ^{0}C and brine (Nacl+KCl) of 24000 TDS, flow rate 2 cc/min).

PV	WATERWEB			AQUACON		
TP	Kw1(md)	Ko1(md)	Kw2(md)	Kw1(md)	Ko1(md)	Kw2(md)
1	0.04	24.8	6.6	18.5	28.3	10.1
2	0.14	28.7	6.5	20.7	39.3	11.4
3	0.71	29.4	6.4	22.4	40.3	12.4
4	2.3	30.2	6.3	23.1	41.2	12.9
5	4.3	30.2	6.1	23.8	41.7	13.1
6	4.7	30.2	5.9	24.2	41.9	13.2
7	4.9	30.2	5.6	24.5	41.9	13.3
8	5.1	30.2	5.1	24.6	41.9	13.4
9	4.9	30.0	4.8	24.7	41.9	13.7
10	4.9	30.2	4.5	24.8	41.6	13.8
20	4.9	30.2	4.3	24.6	41.9	13.8
30	4.9	30.2	4.3	24.6	41.9	14.0
40	5.0	30.2	4.2	24.6	41.9	13.8
50	4.9	30.2	4.2	24.5	41.9	13.8
75	4.9	30.2	4.2	24.6	42.0	13.8
100	4.9	30.2	4.2	24.6	41.9	13.8

Table a2: Post treatment *Kw&Ko* versus injected PV for the tested chemicals in Wanaea cores (T=110 ^{0}C and brine (Nacl+KCl) of 24000 TDS, flow rate 2 cc/min).

PV	Reltreat			RAC		
TP	Kw1(md)	Ko1(md)	Kw2(md)	Kw1(md)	Ko1(md)	Kw2(md)
1	16.6	35.6	8.7	24.8	40.0	7.5
2	18.4	37.0	8.9	26.8	43.3	7.6
3	19.4	43.4	9.0	27.3	47.0	7.7
4	19.4	43.7	9.0	27.3	49.5	7.6
5	18.4	46.5	9.1	27.0	53.3	7.6
6	18.4	46.5	9.2	26.8	52.3	7.6
7	18.4	48.6	9.2	26.1	57.6	7.5
8	18.4	49.4	9.3	26.1	60.8	7.5
9	18.4	50.5	9.3	26.1	60.8	7.5
10	18.4	50.5	9.4	26.1	62.8	7.4
20	16.6	61.5	9.5	26.1	73.6	7.3
30	14.6	67.9	9.5	25.9	78.8	7.2
40	14.1	74.0	9.5	25.9	68.2	7.1
50	14.1	77.6	9.4	25.9	70.8	7.1
75	14.1	85.7	9.4	25.9	73.6	7.1
100	14.1	93.1	9.4	25.9	74.6	7.1

Table a3: Post treatment *Kw&Ko* versus injected PV for the tested chemicals in Berea cores (T=750 ^{0}C while Kw3 performed at 125 ^{0}C, brine (Nacl) of 24000 TDS, flow rate 2 cc/min).

PV	Che-1				Em-1			
TP	Kw1 (md)	Ko1 (md)	Kw2 (md)	Kw3 (md)	Kw1 (md)	Ko1 (md)	Kw2 (md)	Kw3 (md)
0.1	1.38	3.65	1.51	0.74	2.96	4.5	3.44	5.18
0.3	1.41	4.01	1.45	0.78	3.02	5.86	3.93	5
0.4	1.44	4.52	1.4	0.79	3.12	6.4	3.81	4.92
0.5	1.46	5.04	1.38	0.8	3.2	6.95	3.93	4.88
0.7	1.48	5.53	1.35	0.8	3.17	7.93	3.7	4.85
1	1.5	6.41	1.33	0.81	3.24	10.85	4.04	4.8
2	1.52	7.33	1.34	0.82	3.41	12.84	4.15	4.71
3	1.51	8.72	1.35	0.82	3.46	14	4.11	4.53
4	1.52	8.81	1.34	0.83	3.45	14.39	4.3	4.45
5	1.52	9.58	1.36	0.83	3.35	15	4.26	4.38
6	1.53	9.6	1.35	0.84	3.33	15.4	4.34	4.32
7	1.54	9.88	1.34	0.85	3.3	17.1	4.38	4.33
8	1.53	10.1	1.34	0.83	3.19	17.9	4.37	4.35
9	1.52	10.65	1.33	0.81	3.14	18.6	4.37	4.28
10	1.54	10.8	1.33	0.81	3.11	18.9	4.31	4.15
12	1.54	11.65	1.31	0.81	3.01	18.9	4.24	4.08
14	1.51	12.18	1.32	0.82	2.95	18.5	4.1	3.9
16	1.55	12.43	1.32	0.81	3	18.6	4.09	3.81
20	1.56	12.71	1.3	0.84	3.04	19.4	4.14	3.82
25	1.6	13	1.31	0.86	3.08	20.1	4.13	3.88
30	1.56	13.1	1.32	0.85	3.06	20.6	4.13	3.86
40	1.53	13.13	1.31	0.855	3.07	20.51	4.08	3.87

Table a4: Post treatment *Kw&Ko* versus injected PV for the tested chemicals in Berea cores (T=750 ^{0}C while Kw3 performed at 125 ^{0}C, brine (Nacl) of 24000 TDS, flow rate 2 cc/min).

PV	Che-2				Sequential injection SCh-1, SCh-2 & Reltreat			
TP	Kw1 (md)	Ko1 (md)	Kw2 (md)	Kw3 (md)	Kw1 (md)	Ko1 (md)	Kw2 (md)	Kw3 (md)
0.1	5.31	56.88	9.01	4.75	0.95	13.12	0.94	1.68
0.3	4.96	65.4	7.28	4.66	1.23	12.95	0.95	1.73
0.4	4.82	52.3	6.09	4.69	1.25	12.2	0.95	1.82
0.5	4.8	40.1	5.49	4.59	1.25	12.4	0.96	1.88
0.7	4.7	24.2	5.35	4.47	1.26	11.88	0.97	1.95
1	4.71	16.9	5.27	4.4	1.24	11.81	0.98	2.02
2	4.71	16.6	4.87	4.17	1.25	10.8	1.06	2.04
3	4.64	19.1	4.65	4.11	1.27	11.4	1.09	2.03
4	4.68	17.14	4.5	4.08	1.3	13.1	1.19	2.15
5	4.8	15.16	4.4	4.12	1.28	13.3	1.16	2.14
6	4.7	16.21	4.3	4	1.26	12.4	1.24	2.22
7	4.85	16.1	4.3	3.97	1.26	12.86	1.22	2.24
8	5.03	15.9	4.3	3.72	1.29	14.6	1.36	2.23
9	5.61	17.1	4.18	3.45	1.34	14.6	1.54	2.16
10	5.73	16.84	4.13	3.3	1.32	14.8	1.63	2.14
12	5.95	16.2	4.19	3.07	1.3	15.1	1.77	2.13
14	6	17.7	3.32	2.88	1.31	15.2	1.84	2.15
16	5.9	18.4	3.06	2.88	1.33	14.4	1.82	2.18
20	5.85	19.4	3.13	2.84	1.28	15.8	1.83	2.12
25	5.82	19.3	3.25	2.73	1.28	16.1	1.81	2.16
30	5.78	19.6	3.28	2.73	1.26	16	1.8	2.19
40	—	—	—	—	1.28	15.91	1.81	2.18

Table a5: Post treatment *Kw* of different brines versus injected PV through Berea core (B-4) where Che-1 was in situ (T=750 ^{0}C and 125 ^{0}C, flow rate 2 cc/min).

PV	Che-1(T=75C^0)				Che-1(T=125C^0)			
TP	Sa-1 (md)	Sa-21 (md)	Sa-3 (md)	Sa-4 (md)	Sa-1 (md)	Sa-21 (md)	Sa-3 (md)	Sa-4 (md)
0.1	6.32	7.09	7.90	7.49	7.51	9.17	11.95	15.24
0.3	6.10	6.68	7.53	7.54	7.45	9.55	13.36	14.96
0.4	6.40	6.89	7.65	7.61	7.41	9.88	12.70	14.57
0.5	6.25	6.84	7.65	7.62	7.36	10.38	13.70	14.40
0.7	6.00	6.84	7.78	7.72	7.15	9.88	14.03	14.48
1	6.08	6.84	7.94	7.69	6.99	9.59	13.74	14.11
2	6.16	6.64	7.65	7.86	6.86	10.67	13.90	13.90
3	6.12	6.28	7.21	7.88	7.25	10.20	14.30	13.86
4	6.30	6.72	7.70	7.96	7.62	10.92	14.11	13.82
5	6.16	6.24	7.33	7.93	7.63	10.13	13.90	14.19
6	6.24	6.28	7.78	7.92	7.82	10.20	13.94	13.74
7	6.24	6.28	7.37	7.94	7.89	10.20	13.90	13.99
8	6.20	6.65	7.58	7.98	7.68	10.80	14.23	14.48
9	6.16	6.61	7.53	7.93	7.66	10.73	14.69	14.40
10	6.24	6.69	7.63	8.03	7.92	10.38	15.13	13.99
12	6.24	6.69	7.63	8.03	7.73	10.67	15.13	14.19
14	6.12	6.56	7.48	7.85	7.77	10.66	14.84	14.73
16	6.28	6.74	7.68	8.09	7.82	10.67	15.23	14.82
20	6.44	6.78	7.73	7.96	7.93	10.71	15.40	14.82
25	6.48				7.52			
30	6.44				7.96			
40	6.44				7.94			

Table a6: Post treatment *Kw* at different flow rate versus injected PV through Berea core (B-4) where Che-1 was in situ (T=750 ^{0}C, brine NaCl of 24000 TDS, flow rate 2 cc/min).

PV	Che-1 Flow rate(Increasing rate)					Flow rate (Decreasing rate)			
TP	2 cc/min	3 cc/min	4 cc/min	5 cc/min	6 cc/min	5 cc/min	4 cc/min	3 cc/min	2 cc/min
0.2	5.71	6.53	8.37	10.68	14.44	14.00	11.22	8.84	7.11
0.4	5.66	7.19	8.00	11.27	13.85	13.65	11.47	8.90	7.39
0.8	5.57	7.25	8.51	11.80	14.97	13.71	10.15	8.51	7.39
1	5.55	7.45	8.70	12.07	15.43	13.71	11.14	8.11	7.54
2	5.66	7.32	9.30	12.13	15.36	13.12	10.15	8.00	7.54
3	5.66	6.92	9.49	12.13	15.49	12.92	10.42	7.85	7.50
4	5.74	6.86	9.36	12.40	15.43	12.92	10.35	7.91	7.74
5	5.65	6.86	9.49	12.40	15.23	12.79	9.96	7.91	7.70
6	5.65								7.67
7	5.63								7.47
8	5.55								7.45
9	5.57								
10	5.54								

Table a7: Post treatment *Kw* of different brine's pH versus injected PV through Berea core (B-1) where Che-1 was in situ (T=750 ^{0}C, brine NaCl of 24000 TDS flow rate 2 cc/min).

PV	Che-1		
TP	Kw1 pH=8.86	Kw1 pH=12.2	Kw1 pH=41.1
0.1	1.79	2.66	2.44
0.3	1.83	2.83	2.30
0.4	1.88	3.06	2.28
0.5	1.88	2.95	2.09
0.7	1.90	3.04	2.09
1	1.91	3.14	2.13
2	1.90	3.09	2.18
3	1.91	3.04	2.25
4	1.87	2.88	2.23
5	1.86	2.83	2.27
6	1.88	2.88	2.28
7	1.88	3.09	2.39
8	1.91	3.06	2.11
9	1.97	2.95	2.16
10	2.00	2.90	2.13
12	2.00	2.90	2.16
14	1.96	2.94	2.15
16	2.01	2.88	2.20
20	2.03	2.97	2.27
25	2.01		
30	2.00		
40	2.03		

Table a8: Pressure difference across Berea cores during single chemical injection (T=750 ^{0}C, flow rate 2 cc/min).

Che-1		Em-1		Che-2	
PV (Sec)	Δp	PV (Sec)	Δp	PV (Sec)	Δp
8	93.05	8	83.2	8	25.1
100	91.01	100	74.8	100	26.46
200	92.67	200	77.72	200	28.6
300	95.22	300	83.1	300	29.39
400	97.55	400	87.3	400	29.9
500	98.85	500	88.95	500	30.2
600	98.89	600	88.96	600	31
700	98.68	700	91.25	700	31.7
800	101.36	800	91.68	800	31.7
900	99.36	900	93.97	900	31.4
1000	100.96	1000	95.84	1000	31.3
1100	100.94	1100	99.2	1100	30.8
1200	101.96	1200	100.6	1200	31.6
1300		1300	100.8	1300	31
1400		1400	100.31	1400	31
1500		1500	99.84	1500	30.4
1600		1600	100.6	1600	30.5
1700		1700	100.19	1700	30.6
1800		1800	103.4	1800	29.9
1900		1900	105.8	1900	30.1
2000		2000	103.52	2000	30.05
2100		2100	104.89	2100	30.4
		2200	105.78		
		2300	103.96		
		2400	105		
		2500	103.82		
		2600	106.2		
		2700	106.6		
		2800	109.1		

Table a9: Two phase flow tests versus injected pore volume.

Two phase flow test: where Che-1 was in situ. T=75						
PV	Time of measurement	Oil produced (cc)	Total produced oil in %	Water produced (cc)	Total produced water in %	Δp
1	5.15	8.1	75.00	2.7	25.00	208.29
2	10.3	8.7	80.56	2.1	19.44	194.91
3	15.45	8.5	78.70	2.3	21.30	206.86
4	21	8.6	79.63	2.2	20.37	235.88
5	26.15	9.3	86.11	1.5	13.89	237.14
6	31.3	8.5	78.70	2.3	21.30	235.67
7	36.45	8.4	77.78	2.4	22.22	238.08
8	42	8.5	78.70	2.3	21.30	240.67
9	47.15	8.4	77.78	2.4	22.22	236.46
10	52.3	8.2	75.93	2.6	24.07	233.28
15	78.45	43.1	79.81	10.9	20.19	237.3
Two phase flow test: where Em-1 was in situ. T=75						
PV	Time of measurement	Oil produced (cc)	Total produced oil in %	Water produced (cc)	Total produced water in %	Δp
1	5.12	6.1	55.45	4.8	43.64	140.1
2	10.24	6.8	61.82	4.1	37.27	146.57
3	15.36	6.5	59.09	4.4	40.00	149.75
4	20.48	7	63.64	3.9	35.45	146.22
5	26	7.1	64.55	3.8	34.55	153.92
6	31.12	6.8	61.82	4.1	37.27	158.72
7		6.7	60.91	4.2	38.18	153.3
8		6.7	60.91	4.2	38.18	152.2
9		6.5	59.09	4.4	40.00	148.9
10		6.6	60.00	4.3	39.09	151.3
12		13.1	59.55	8.9	40.45	150.4
Two phase flow test: where Em-1 was in situ, performed after injecting 3 PV of oil.						
PV	Time of measurement	Oil produced (cc)	Total produced oil in %	Water produced (cc)	Total produced water in %	Δp
1	5.2	2.8	25.45	8.1	73.64	120.6
2	10.4	2.1	19.09	8.8	80.00	122.7
3	16	2.8	25.45	8.1	73.64	121.57
4	21.2	2.2	20.00	8.7	79.09	119.84
5	26.4	1.6	14.55	9.3	84.55	124.5
6	32	1.6	14.55	9.3	84.55	120.6
7	37.2	1.4	12.73	9.5	86.36	128.5
8	42.4	1.8	16.36	9.1	82.73	121.53
9	48	1.5	13.64	9.4	85.45	125.93
10	53.2	2	18.18	8.9	80.91	121.2

Table a10: Pressure difference across B-5 during injecting SCh-1, SCh-2 and Reltreat sequentially.

SCh-1		Reltreat		SCh-2	
PV (Sec)	Δp	PV (Sec)	Δp	PV (Sec)	Δp
8	21.36	408	91.3	712	54.77
16	22.34	416	114.89	720	67.59
24	21.62	424	122.38	728	96.95
32	21.39	432	117.66	736	126.55
40	21.19	440	106.85	744	142.17
48	21.01	448	77.66	752	146.21
56	20.25	456	36.7	760	147.91
64	20.16	464	30.59	768	143.75
72	20.78	472	25.76	776	144.58
80	20.58	480	23.53	784	145.47
88	20.86	488	21.05	792	140.97
96	20.79	496	18.86	800	138.5
104	19.99	504	17.41	808	138.29
112	20.51	512	11.54	816	139.2
120	21.13	520	8.36	824	140.47
128	21.11	528	8.21	832	142.52
136	20.42	536	8.18	840	146.89
144	20.93	544	8.09	848	146.17
152	20.46	552	13.14	856	145.9
160	19.86	560	13.96	864	146.67
168	21.3	568	15.43	872	146.05
176	19.83	576	16.39	880	145.8
184	21.53	584	16.41	888	145.04
192	20.31	592	15.78	896	142.65
200	21.38	600	13.73	904	143.23
208	20.94	608	12.95	912	143.69
216	19.76	616	11.75		
224	20.42	624	12.15		
232	20.21	632	11.98		
240	20.64	640	11.81		
248	19.26	648	11.26		
256	19.67	656	11.49		
264	19.28	664	10.8		
272	19.89	672	10.63		
280	19.55	680	10.73		
288	19.37	688	11.14		
296	19.83	696	9.56		
304	19.19	704	10.36		
312	19.04				
320	18.72				
328	19.32				
336	20				
344	19.31				
352	17.82				
360	18.91				
368	19.32				